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Advances in the application of nanomaterials for natural stone conservation

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Abstract

The unpredictable effects of climate change impose the safeguarding of Cultural Heritage (CH) with effective and durable materials as a vital solution in the invaluable socioeconomic resource of CH. Conservation products and methodologies are addressed under recent advancements in colloidal science providing multi-functional solutions for cleaning, consolidation, protection, and monitoring of the architectural surfaces. Nanoscience significantly contributes to enrich the palette of materials and tools that can guarantee an effective response to aggressive environmental agents. Nanostructured multi-functional nanoparticles, nanostructured fluids, and gels for stone conservation are reviewed and future perspectives are also commented. The stability and high flexibility in designing tailored made nanoparticles according to the specific characteristics of the substrate enable their use in a variety of applications. Stemming from the well-performed in lab applications with nanomaterials, the testing onsite and the monitoring of their effectiveness are of crucial importance, considering also the constructive feedback from conservators and heritage stakeholders that can unquestionably contribute to the improvement and optimisation of the nanomaterials for CH protection.

Keywords: Nanomaterials; Cleaning; Consolidation; Protection; Natural stone

1 Introduction

Over the past decades, the rapid changes in climate and concentrations of air pollutants have been affecting the conservation of stone materials in historical buildings. The rise in the frequency of extreme weather events and precipitations has been accelerating their deterioration, leading to the increase in surface recession and erosion [1, 2]. In addition, some of the materials most used in past interventions, such as acrylates, epoxy resins, polyvinyl acetate, etc., proved not be suitable for the conservation of stone substrates, due to their low compatibility, stability, and retreatability [3, 4]. These polymeric materials tend to fill the pores of natural stones, changing the open porosity, and resulting in changes to the drying and permeability properties. In addition, they often undergo discoloration and change in solubility over time, making their removal more challenging.

In this context, since the ‘80s, the scientific research applied to the conservation of Cultural Heritage (CH) has taken up the technological advances in nanotechnology to develop nanomaterials able to fulfil specific requirements. These tailor-made nanomaterials display high chemical and aesthetical compatibility with the original substrates. Compared to some traditional materials, some classes of nanomaterials show less toxicity and have less impact on human health and the environment [5]. However, limited data about the risks to long-term exposures are available and research in the health and environmental implications of these formulations is ongoing. Sustainability framework based on the safe by design concept can support developers in the assessment of the sustainability of new products to promote the selection of safer and more sustainable materials for conservation [6]. Nanomaterials show improved properties, due to their higher surface area and thus, reactivity (e.g. compared to traditional lime, a reduction of carbonation reaction time occurs with nanolimes) [5]. The possibility to apply a tailor-made approach in the synthesis of these nanomaterials allows for modulation of their reactivity and properties by controlling their particle size and functionalization. Finally, these innovative formulations allow a better control of the release of the products on the surface, improving the selectivity in the treatment of unwanted layers, without compromising the original historic and artistic substrate. In a recent book, an overview of the ongoing research on innovative treatments and methods for stone conservation is showcased [4].

Despite the promising results of these innovative formulations obtained from laboratory tests, only a few studies take into consideration the performance of the

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treatments on naturally weathered stone substrates in trial areas on historical buildings. Changes in the effectiveness of conservation treatments applied onsite are common due to environmental and operational factors, which influence the application methodology and the curing of the products [7].

The following paragraphs will showcase the most recent and promising research studies in the development and application of nanomaterials for cleaning, consolidation, and protection of natural stones, highlighting current trends and future perspectives. This research highlights the fundamental role of the collaboration among different professionals (conservators, architects, scientists, etc.) in the success of conservation treatments for built heritage conservation.

2 Nanomaterials for stone cleaning

Cleaning is considered the most delicate operation in conservation, since it requires high selectivity, is irreversible, has a direct action on the substrate, can lead to the excessive removal of unwanted layers, and eventual release of harmful by-products. Besides aesthetic and durability reasons that impose the cleaning intervention, most of the unwanted substances, such as soiling, dirt, soluble salts, gypsum crusts, pollutants and heavy metals, biological crusts, residues of previously applied treatments, etc., can significantly accelerate the decay process and, therefore, their removal is imperative. Traditional cleaning methods have been proposed using water- and solvent-based systems for softening the layers to be removed, mechanical tools and sandblasting, as well as more advanced laser and plasma tool technology. The methods based on solvent, water, and sandblasting are less selective and poorly controlled often generating side effects due to the excess water ingress and surface material loss [8]. Other issues to be considered when carrying out cleaning interventions are the environmental-friendly and non-toxic characteristics that are required and should be fulfilled for the operators and the environmental safety.

Nanoscience has significantly contributed to the advancement of conservation research in recent years, thanks to pathways investigated in last decades related to the action of nanostructured fluids (NFs), nanogels, magnetically responsive nanogels, and peelable gels [9].

NFs, which are colloidal systems based on micelles solutions and microemulsions, were deliberately proposed to efficiently remove coatings from hydrophilic porous materials [10]. The micelles solutions consist of surfactants, using a combination of water (60-90%, w/w), oil, and a co-surfactant. The microemulsions consist of liquid phases, which are well dispersed with a surfactant and could be either hydrophilic (oil in water) or hydrophobic (water in oil), depending on the cleaning procedure. As described in the literature for lab and *in situ* applications, the NFs are used to remove synthetic polymers, sulphates and chlorides, unwanted graffiti, vinyl and acrylic coatings, polysiloxane-based resin, waxes, polymers, or varnishes, which are difficult to remove with traditional cleaning methods from various substrates, such as Carrara marble, wall painting mock-ups, stucco masks, frescos, canvas, etc. [11-14].

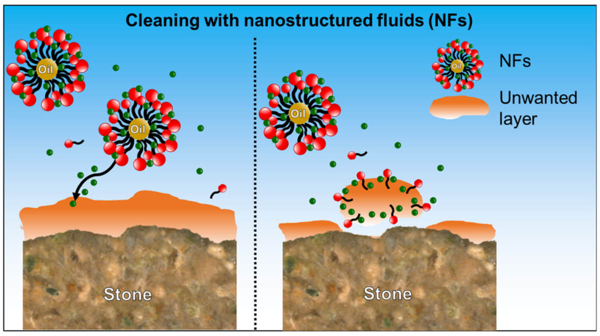

Figure 1. The selective action of aqueous nanofluids (NFs) for the removal of unwanted layers from stone.

Considering that NFs can solubilise the ingredients of the protective materials, they can be considered as an innovative "green" approach in the cleaning of surfaces [12, 15]. NFs serve as solvent containers to interact, swell, and detach the polymer film from the surface, and then to segregate it into a liquid droplet that can be easily phase-separated from the aqueous bulk (see Figure 1). After the polymer removal, the NFs are depleted from the organic solvents, and can easily be detached from the surface. Acrylic polymer (Paraloid B72), silicone-based resin (Dri-Film 104, DF), and their mixture (Bologna Cocktail, BC) were efficiently removed with NFs from artificially deteriorated marble with the aid of a cellulose pulp as it was also confirmed by the analytical techniques used [13, 15, 16]. A cleaning treatment using the oil-in-water emulsion based on the halloysite nanotubes modified with the surfactant sodium dodecyl sulfate (SDS) and tetradecane successfully removed an aged oil-based protective varnish from a marble sculpture [17]. The physico-chemical process underpinning the cleaning effectiveness of NFs is related to the detergency properties of the hydrophobic part of the micelle to solubilise apolar molecules like organic substances and polymers, common constituents of the unwanted layers.

Apart from the unquestionable effectiveness of NFs, physical gels chemically inactive with the substrate, such as polyacrylic acid, as well as thick and stable emulsions of natural polysaccharides like gum and agar capable of holding considerable amounts of water, were also proposed to clean stone surfaces [18]. These gels can remove soiling, grime, and polymers, and can be formulated according to the specific characteristics of the layer that has to be removed. Particular attention should be paid to remove residues of polymer that were eventually accumulated in fissures or other cavities on the surface and could accelerate damage. The cleaning of the marble statue "Fuga in Egitto" in the Milan Cathedral is a prime example of the effective cleaning with agar gels to removing soil, salts, and soot without any detriment to the marble surface [19].

The contribution of nanoscience towards the advancement of physical gels is expressed by the nanogels formulation, which includes synthetic hydrophilic polymeric networks or biopolymers chemically or physically crosslinked. The nanogels with diameters of up to hundreds of nanometers have many advantages, as they can embed a variety of liquid media, spanning from organic solvents, to NFs, aqueous solutions with enzymes or chelates, etc., and they can have successful applications in a vast range of materials apart from works of art [20]. The nanogels slowly release the cleaning agents at the interface, thus reducing the underlying layer swelling and the ingress into the pores of the material. On the other hand, the high viscosity of the nanogels better controls the interaction with the substrate, decreases the solvent evaporation rate, and the whole operation becomes more selective. Finally, the chemical structure of the formulation of nanostructured gels allows for a quick, complete, and non-invasive removal through the aid of weak acidic solutions that change it into a liquid state easily removable with dry cotton swabs [21].

Advancements in the nanogel system involved the use of magnetic nanoparticles and oil-in-water microemulsions to produce a magnetically responsive gel-system that will attract the unwanted substance from the surface of a material [22]. This system solubilises the polymer, captures its components, and incorporates them into the gel's structure. A marble surface treated with Paraloid B72, besides the aging of polymer, was effectively cleaned by applying a microemulsion-loaded magnetic gel consisting of polyacrylamide with ferrite magnetic nanoparticles, for about 2 hours [22].

Another group of nanogels involved in advanced cleaning interventions are the peelable gels, which show high intrinsic elasticity that allows them to be easily removed by peeling, without leaving residues on the treated surface. They can be loaded with both aqueous cleaners and organic solutions, making them effective in a wide range of materials with different physicochemical properties [23]. The addition of a polyvinyl alcohol or a network of polyvinyl-1-pyrrolidone and poly(2-hydroxyethylmethacrylate) as gellants are factors responsible for the peelability. An acrylic coating from porous limestone was effectively removed with the aid of a polyvinyl alcohol-borax and poly(ethylenoxide), which supported the shape of the hydrogel and increased the relaxation time [24].

The nanogel group also includes the semi-interpenetrating peelable gels characterised by a high-water retention ability and mechanical properties, which enable them to be used on water-sensitive surfaces. Generally, a hydrogel formulation with the proper microemulsion in qualitative and quantitative terms can sufficiently remove aged polymers from stone surface [9]. Different formulations of hydrogels holding microemulsions versus pure organic solvents were tested for the removal of Paraloid B72, polyvinyl acetate, and silicone acrylics, taking into consideration the control of the treatment and the protection of the treated surfaces [25]. Furthermore, poly (vinyl) alcohol-borax hydrogels containing silver nanoparticles with antimicrobial properties were tested over two biodeteriorated stones, namely Carrara marble and St. Margarethen limestone, offering a natural solution to contamination mitigation [26].

Cleaning with traditional pure organic solvents should be avoided due to their rapid infusion into the stone and to capillary forces that cause severe damage to the surface, swelling, softening, and leaching. To avoid those drawbacks, the use of flocculent systems, such as nanogels and NFs is an effective alternative intervention for the removal of polymer coating and dirt from stone surfaces. However, it should be mentioned that the particularly demanding design and application of NFs and nanogels make them a non-cost-effective procedure for the cleaning of large areas.

3 Nanostructured materials for stone consolidation

Consolidation treatments for stone materials aim to "re-establish totally or partially the cohesion loss, while keeping the impact of any foreseeable negative side effect at its possible minimum" [27]. In the '90s nanolime was first synthesised and applied in heritage conservation, in order to overcome some of the drawbacks of limewater, which has been used to consolidate limestones and plasters for centuries (Figure 2). Nanolime consists of a water/alcoholic dispersion of calcium hydroxide ($Ca(OH)_2$) nanoparticles in concentrations of 5-50 g/L, with sizes between 50 and 600 nm [28]. When exposed to atmospheric CO_2 at room temperature and in the presence of water, they carbonate, forming $CaCO_3$ cement that binds decayed stone or wall paintings [29]. During carbonation, $CaCO_3$ nuclei are formed in the boundary regions of the $Ca(OH)_2$ particles, followed by thickening of slab-like regions centered on the original boundaries [30]. During the reaction, amorphous calcium carbonate (ACC) is firstly formed, followed by metastable phases (vaterite and minor aragonite), via a dissolution–precipitation process, followed by nonclassical nanoparticle-mediated crystal growth. Finally, vaterite undergoes partial dissolution, while stable calcite precipitates [30]. Due to its nanostructured size and higher specific surface area, nanolime displays several advantages compared to traditional limewater: higher colloidal stability and good penetration into the stone pores, reducing the formation of white surface stains [31]; the avaialbility of several synthesis routes to fine-tune the particle size and control the reactivity and surface properties [32, 33]; and higher reactivity resulting in a beneficial reduction of the carbonation time. Since the introduction of different commercial products, nanolimes have been widely applied for the consolidation of limestones [28, 32, 34-41], lime mortars [35, 42-45], and wall paintings [32, 46]. The selection of the concentration and type of solvent of the suspension and of the application methodology are important factors to consider prior to the conservation intervention. In addition, the environmental conditions (relative humidity and temperature) during the application and curing of the products can affect their effectiveness [32, 43]. Nanolimes require a slow and accurate application to the substrates, as they can easily impregnate the most superficial layers, resulting in the formation of an instable and hard crust and whitening due to surface deposition [27]. Despite being on the market for several years, only limited results on the durability of nanolime treatments applied onsite on naturally aged stone surfaces are available [28, 39, 40, 47].

In 2011, Sassoni et al proposed a new consolidation treatment for limestone and marble based on the use of hydroxyapatite and calcium phosphates as an improved alternative to the ammonium oxalate treatment, which produces calcium oxalates with similar solubility of calcite in water [48]. Instead, the new treatment focuses on the application of an aqueous solution of ammonium phosphate salts (with diammonium hydrogen phosphate being the most used), which reacts with calcite in the stone, forming new calcium phosphate phases (ideally, hydroxyapatite) inside the cracks or on the stone surface [49]. This results in improved mechanical properties due to the increase of the cohesion among calcite grains and higher resistance of the substrates to dissolution once exposed to acidic solutions, as hydroxyapatite has solubility and dissolution rates much lower than those of calcite. In most of these studies, hydroxyapatite was produced *in situ*, instead of using dispersion of already-formed nanocrystals [50-53]. Compared to other traditional consolidation treatments (ethyl silicate and ammonium oxalate), this product proved to be very effective on weathered marble and limestones, due to its good penetration in the pores (reaching at least 20 mm depth), short curing time, without affecting the porosity, pore-size distribution of the substrates, the hydrophilicity and water absorption properties, and the surface colour. Once applied on weathered stones onsite, good consolidation results were obtained in the treatments of a marble gravestone [54], a marble byzantine sarcophagus [55], and a Hellenistic-Roman tomb in marlstone from Cyprus [56]. Promising results were also obtained from a 3-year monitoring program of naturally weathered marble specimens and a 17th century marble sculpture from the Park of the Royal Palace in Versailles (France), proving that some of the phosphate-based materials were able to hinder marble deterioration [57].

The most used consolidants for carbonate stones and sandstones are alkoxysilanes, especially tetraethyl orthosilicate (TEOS), as they display good penetration depth in the stone pores, chemical stability, and they don't affect the water vapour permeability properties of natural stone. However, alkoxysilanes bond poorly to calcite crystals, have long curing time (about 4 weeks), and tend to shrink and crack during drying and solvent evaporation. To reduce the gel brittleness, particle-modified consolidants (PMC) have been proposed, by introducing different nanoparticles (SiO_2, TiO_2, Al_2O_3, etc.) in pre-polymerised TEOS [58-62]. PMC have been applied on several lithotypes and they proved to be able to increase the elastic modulus and reduce the thermal expansion coefficient, leading to a significantly reduced degree of gel cracking. Hydroxyapatite nanoparticles and amylamine-based surfactant have been introduced in TEOS solution to reduce the capillary pressure of the gel during drying, and led to improved tensile strength and drilling resistance once applied on limestone samples [63]. Good penetration depth and consolidation effectiveness of carbonate stone were also achieved by adding hydroxyapatite nanorods and silica nanocrystals to TEOS [64].

Another interesting example of PCM consists of the incorporation of calcium oxalate monohydrate nanoparticles in TEOS to form a crack-free nanocomposite which can be used for the consolidation of carbonate stones and cement mortars [65, 66]. This nanocomposite was developed by integrating calcium oxalate nanoparticles into the silica matrix, to form a crack-free gel, in which the nanoparticles can foster the chemical affinity between the silica network and the carbonate substrate. Natural calcium oxalate patina developed on some well-preserved monuments and historical buildings over time has proved to play a role in the protection of the stone surfaces, therefore, this nanocomposite exhibits both consolidation and protective features. The nanocomposite reached a good penetration depth inside the stone, without affecting the porosity and pore size distribution, with an improvement of the tensile strength. A further advancement of this formulation was the addition of polydimethylsiloxane (PDMS) to obtain hybrid hydrophobic consolidants, resulting in an increase in the resistance to decay and enhanced mechanical properties of the limestone [67].

Due to their nanometric size, suspensions of silica nanocrystals have been proposed as alternatives to alkylsilicate-based consolidants to achieve a deeper penetration in the stone pores and reduce the curing time. Nanosilica dispersions (maximum 55 nm size) were applied to a limestone characterised by pore sizes ranging 0.5 and 5 µm, but they accumulated on the surface forming a xerogel, with penetration up to 2 mm into the substrate [68]. Ethanol-water solutions of nano-silica with different particle sizes compatible to the pore size distribution of granite and sandstones under study resulted in poor penetration in the substrates. Different commercial products are available, and some studies reported that their consolidation effectiveness and durability is deeply influenced by environmental parameters, in particular, relative humidity [69, 70]. Promising results were obtained by the application on a porous limestone of a commercial colloidal dispersion of nanosized SiO_2, which was formulated for the consolidation of the marble capitals of the Leaning Tower of Pisa (Italy) [71]. Further optimisation of the formulations will aim to improve the application methodology of the product to achieve a better distribution within the stone pores.

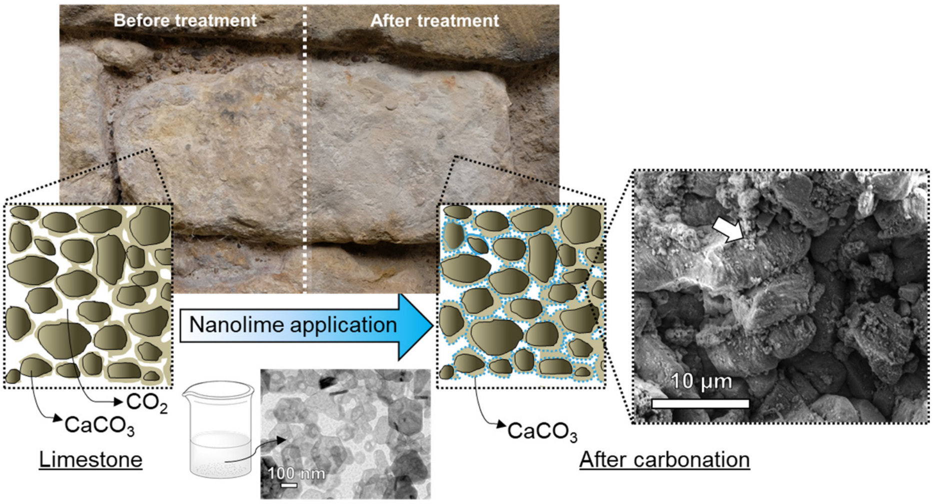

Figure 2. Lincolnshire limestone before and after the treatment with nanolime. Schematic representation of the application of calcium hydroxide nanoparticles (Transmission Electron Microscopy image), the formation of calcium carbonate after the reaction with carbon dioxide, and Scanning Electron Microscopy image of the consolidated stone.

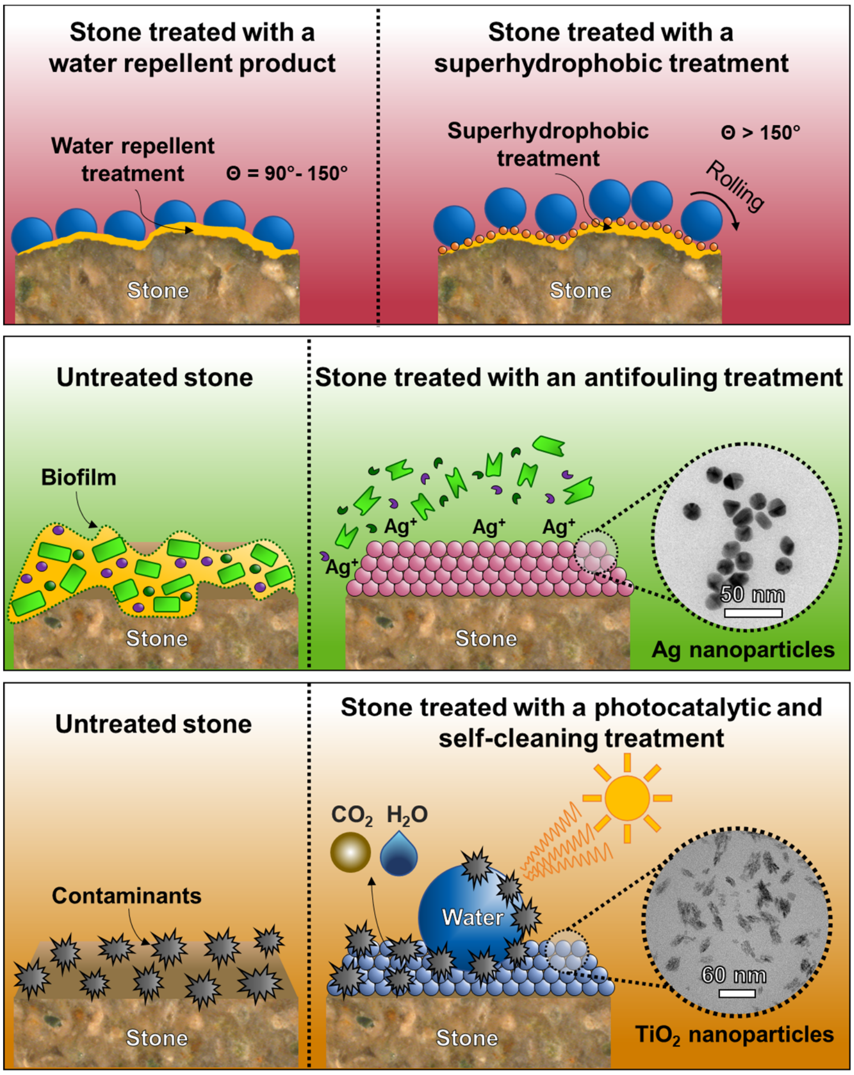

Figure 3. Top row: static contact angle (Θ) of a water drop on a stone surface treated with a water repellent product and with a superhydrophobic treatment. Middle row: schematic representation of biofilm deposition on untreated stone surfaces and the antifouling properties of surfaces treated with silver (Ag) nanoparticles, and Transmission Electron Microscopy (TEM) image of the nanoparticles. Bottom row: schematic representation of contamination of stone surfaces by pollutants and the photocatalytic and self-cleaning properties of surfaces treated with TiO_2 nanoparticles, and TEM image of the nanocrystals.

Since prehistoric times, earth and clay have been widely used in buildings and archaeological sites. Clay-based building materials include mud-bricks, clay-plasters, cob, and rammed earth, and their use spread thanks to the wide availability, low cost, and environmental impact [72, 73]. However, these materials are very vulnerable to water-related decays such as wind-driven rain, soluble salt crystallization, wetting and drying, and freeze-thaw cycles. In addition, humidity plays a crucial role in regulating swelling and shrinking of clay minerals and it can significantly compromise the cohesion of the structure and its mechanical properties. To solve this issue, alkaline treatments were applied to clay-based materials with the aim to reduce the swelling of the minerals [74]. Among nanomaterials, nanolimes are promising swelling inhibitors for the consolidation of clay structures, as they can react and dissolve the alumino-silicate clay minerals and form calcium silicate hydrate (C-S-H) phases. These pozzolanic phases were able to increase the durability of mud bricks from the prehistoric settlement of Thessaloniki Toumba (Greece) [75]. Promising results were also obtained by applying a formulation prepared by combining $Ca(OH)_2$ and SiO_2 nanoparticles with hydroxypropyl cellulose, for the consolidation of adobe bricks [76]. This nanocomposite was able to form C-S-H *in situ*, resulting in enhanced resistance to peeling, abrasion, and wetting and drying cycles.

4 Nanostructured protective treatments for stone

Nanoparticles with different properties (self-cleaning, depolluting, antifouling, etc.) have been applied to stone substrates either in water/solvent dispersions or introduced in polymeric or inorganic compounds.

Nanocrystals have been embedded in polymers to obtain hybrid nanocomposites able to improve the protection effectiveness and increase the hydrophobicity of the treated substrates. Indeed, the presence of nanoparticles in the coatings enhances the surface roughness, without modifying the substrate morphology, and produces improved water repellency. The treated surfaces interact with rainfall, producing water spherical droplets which roll away, embedding and removing dusts and particles, making the surface superhydrophobic (water static contact angle > 150°) (Figure 3). In addition to superhydrophobicity, the treated surfaces can exhibit superoleophobic and oil repellent properties. Different polymers (acrylates, fluorinated polymers, and siloxanes) and nanoparticles (silica, alumina, titania, etc.) have been used to developed formulations with additional functional properties (photocatalytic and self-cleaning), which were tested on several stone substrates [77-79]. The high flexibility of this methodology allows for the modification of the surface roughness by selecting the most appropriate concentration of nanoparticles in the formulations, according to the features of the stones. In particular, promising results from laboratory tests were obtained on siloxane-based treatments applied on sandstones and marbles [79]. The study of these formulations after accelerated ageing tests, onsite application in historical buildings, and the monitoring of their performance over time will provide crucial data on their durability [80].

To reduce the biodeterioration of stone substrates, antifouling treatments have been designed by using nanostructured metal oxides, such as silver (Ag), copper (Cu), zinc oxide (ZnO), and titanium oxide (TiO_2) (Figure 3). [81]. Silver nanocrystals have good antimicrobial properties, as they can affect microbial cellular metabolic processes and inhibit protein synthesis and DNA replication due to the release of Ag^+ ions, leading to the destruction of bacterial cell walls and membranes. Good results in the inhibition of biofilm formation have been obtained by silver nanoparticles combined with a silane-based grafting agent applied on Serena stone [82] and by dispersions of citrate-capped silver and titania nanoparticles on limestones [83]. A product based on hydrophobised silica with silver and zinc oxide nanoparticles was applied on stone substrates with different open porosity and pore size distribution, and it displayed good antibacterial and protective properties even after accelerated ageing [84].

A nanocomposite based on ethyl silicate and polysiloxane oligomers and copper nanoparticles was effective in reducing the biological colonization over time, due to a continuous and controlled release of biocide copper ions on the stone [85]. An important aspect to consider with formulations with silver and copper nanoparticles is their concentration, in order to avoid significant alteration of the surface colour of the substrates.

In addition to photoactivity, zinc oxide nanoparticles display antibacterial and antifungal properties, due to the toxic release of zinc ions in the environment [81]. Zinc oxide combined with dispersions of calcium hydroxide particles and nano-titania showed antifungal properties [86]. Nanocomposites based on nano-ZnO and tetraethoxysilane and polysiloxanes applied on different calcareous stones resulted in the reduction and prevention of biofilm formation over time [87].

Another approach includes the use of silica nanocapsules which can gradually release biocides to the stone surface. These nanocontainers can be loaded with biocides such as zosteric sodium salt [88] or essential oils [89], reducing the amount of biocide in antifouling coatings.

Thanks to their availability, high chemical and thermal stability, low toxicity and cost, titania nanoparticles are the most used semiconductor, for self-cleaning and depolluting applications in several fields (Figure 3). Titania crystallises in three forms: anatase, rutile, and brookite, being rutile and anatase the most used, due to their higher photoactivity and stability. When exposed to UV light or solar radiation, titania absorbs photons, producing pairs of electrons and holes. Reactive oxygen species are formed from molecules in the atmosphere on its surface, promoting the decomposition of organic molecules, and the oxidation or reduction of inorganic compounds. In addition, titania has also antifouling properties, as the reactive species can also oxidise the cell membrane of microorganisms. Titania nanoparticles also display also superhydrophilic features, as they can adsorb OH^- groups on the surface, which, in turn, adsorb water and prevent the contact between the surface and the contaminants. In this way, the surface becomes "self-cleaning", as soiling and degraded pollutants are easily removed.

Treatments with nano-TiO_2 include dispersions in different solvents, which have been applied on compact limestones, marble, and travertine, without modifying the natural hydrophilic properties of stone substrates [90, 91]. However, nanoparticles can be easily removed by rain-wash due to their poor adhesion to the substrate, thus reducing the effectiveness of the treated surfaces. To anchor the nanoparticles to the surface, avoid their leaching, and penetration in the stone pores, layered treatments based on tetraethyl orthosilicate and nano-TiO_2 were proposed and successfully tested on a porous calcarenite and marble [92].

Nanocomposites can be prepared by embedding the nanoparticles in a polymeric or inorganic compound, improving their adhesion and the homogenous dispersion on the stone surface. Silanes and polysiloxanes, fluorinated or partially fluorinated polymers, and acrylics have been used to design hydrophobic coatings [93-97], and some of them were conceived for stone consolidation and protection [98-100]. One of the challenges of polymer-based nanocomposites is to find the right nanoparticle concentration to use in order to achieve a balance between high photoactivity and stability of the formulations, as the polymeric matrix can be degraded [101]. Another approach to graft titania nanoparticles to the surface, without changing the hydrophilicity, is to disperse them in hydroxyapatite coatings [102]. Little data are available about the long-term durability after the natural weathering of TiO_2-based nanocomposites. Laboratory studies were carried out to assess the durability of treatments with nano-TiO_2 [103-106]. After few accelerated weathering cycles, only the treatments prepared by adding nanoparticles in polymeric and inorganic binders still displayed photoactivity. Despite being subjected to photochemical degradation, the polymeric nanocomposite retained photocatalytic and protective properties, and the alkyl-silica matrix was able to anchor the nanoparticles to the surface and provide resistance to rain-wash [106]. Results from field exposure of limestone samples treated with photocatalytic nanocomposites proved that the treatments were able to reduce soiling accumulation [107]. In another study, after being exposed to natural weathering for 12 months, dispersion of nano-titania showed poor adhesion to the marble substrate, resulting in low photocatalytic efficiency [108]. Different formulations of nano-TiO_2 treatments were applied on marble slabs on the façade of Monza Cathedral (Italy) and monitored for 12 months. The treatments displayed good compatibility and protection, but a long-term monitoring of the treated areas will be required to assess their durability [109].

5 Conclusions

This review comprises recent advances in the development of nanostructured treatments for cleaning, consolidation, and protection of natural stones in built heritage. Nanotechnology allows high flexibility in the functionalisation of the nanoparticles, to improve their interaction with the stone substrate, their stability, and their properties. In this way, it is possible to tailor the treatments according to the characteristics of the specific case-study. Promising results have been obtained by laboratory studies, especially in the cases of cleaning requiring maximum selectivity of the treatment and in surface protection providing multi-functional products with self-healing and self-cleaning properties. However, to evaluate their suitability for the conservation of architectural heritage and their durability, it is crucial their application and testing are implemented onsite, and to monitor their effectiveness over time. In this way, constructive feedbacks from conservators and heritage stakeholders can be used to improve and optimise the products.

The possibility to study the change in the properties of these treatments in models that simulate future scenarios will demonstrate their significant impact on the durability of the built heritage and on the mitigation of possible detrimental climate change effects.

Authorship statement (CRediT)

Francesca Gherardi: conceptualisation, writing – original draft, writing – review and editing.

Noni Pagona Maravelaki: conceptualisation, writing – original draft, writing – review and editing.

References

[1] Sesana E, Gagnon AS, Ciantelli C, Cassar J, Hughes JJ, Climate change impacts on cultural heritage: A literature review WIREs Climate Change (2021) 12(4):e710. https://doi.org/10.1002/wcc.710

[2] Basu S, Orr SA, Aktas YD, A Geological Perspective on Climate Change and Building Stone Deterioration in London: Implications for Urban Stone-Built Heritage Research and Management Atmos (2020) 11(8):788. https://doi.org/10.3390/atmos11080788

[3] Favaro M, Mendichi R, Ossola F, Russo U, Simon S, Tomasin P, Vigato PA, Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part I: Photo-oxidative weathering Polym Degrad Stab (2006) 91(12):3083-3096. https://doi.org/10.1016/j.polymdegradstab.2006.08.012

[4] Favaro M, Mendichi R, Ossola F, Simon S, Tomasin P, Vigato PA, Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part II: Photo-oxidative and salt-induced weathering of acrylic-silicone mixtures Polym Degrad Stab (2007) 92(3):335-351. https://doi.org/10.1016/j.polymdegradstab.2006.12.008

[5] Baglioni P, Carretti E, Chelazzi D, Nanomaterials in art conservation Nat Nano (2015) 10(4):287-290. https://doi.org/10.1038/nnano.2015.38

[6] Semenzin E, Giubilato E, Badetti E, Picone M, Volpi Ghirardini A, Hristozov D, Brunelli A, Marcomini A, Guiding the development of sustainable nano-enabled products for the conservation of works of art: proposal for a framework implementing the Safe by Design concept Environ Sci Pollut Res (2019) 26(25):26146-26158. https://doi.org/10.1007/s11356-019-05819-2

[7] Gherardi F, Maravelaki PN. Conserving Stone Heritage: Traditional and Innovative Materials and Techniques. Springer International Publishing; 2022. https://doi.org/10.1007/978-3-030-82942-1

[8] Maravelaki PN, Surface Cleaning: Implications from Choices & Future Perspectives. In: Gherardi F, Maravelaki PN, editors. Conserving Stone Heritage: Traditional and Innovative Materials and Techniques. Cham, Springer International Publishing, 2022, 37-74. https://doi.org/10.1007/978-3-030-82942-1_2

[9] Baglioni M, Poggi G, Chelazzi D, Baglioni P, Advanced Materials in Cultural Heritage Conservation Molecules (2021) 26(13). https://doi.org/10.3390/molecules26133967

[10] Baglioni P, Berti D, Bonini M, Carretti E, Dei L, Fratini E, Giorgi R, Micelle, microemulsions, and gels for the conservation of cultural heritage Adv Colloid Interface Sci (2014) 205:361-371. https://doi.org/10.1016/j.cis.2013.09.008
[11] Domingues J, Bonelli N, Giorgi R, Baglioni P, Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings Appl Phys A (2014) 114(3):705-710. https://doi.org/10.1007/s00339-013-8150-0
[12] Carretti E, Dei L, Baglioni P, Solubilization of Acrylic and Vinyl Polymers in Nanocontainer Solutions. Application of Microemulsions and Micelles to Cultural Heritage Conservation Langmuir (2003) 19(19):7867-7872. https://doi.org/10.1021/la034757q
[13] Baglioni M, Jáidar Benavides Y, Desprat-Drapela A, Giorgi R, Amphiphile-based nanofludis for the removal of styrene/acrylate coatings: Cleaning of stucco decoration in the Uaxactun archeological site (Guatemala) J Cult Herit (2015) 16(6):862-868. https://doi.org/10.1016/j.culher.2015.03.008
[14] Baglioni M, Raudino M, Berti D, Keiderling U, Bordes R, Holmberg K, Baglioni P, Nanostructured fluids from degradable nonionic surfactants for the cleaning of works of art from polymer contaminants Soft Matter (2014) 10(35):6798-6809. https://doi.org/10.1039/C4SM01084A
[15] Grassi S, Favaro M, Tomasin P, Dei L, Nanocontainer aqueous systems for removing polymeric materials from marble surfaces: A new and promising tool in cultural heritage conservation J Cult Herit (2009) 10(3):347-355. https://doi.org/10.1016/j.culher.2008.10.003
[16] Baglioni M, Alterini M, Chelazzi D, Giorgi R, Baglioni P, Removing Polymeric Coatings With Nanostructured Fluids: Influence of Substrate, Nature of the Film, and Application Methodology Frontiers in Materials (2019) 6. https://doi.org/10.3389/fmats.2019.00311
[17] Lo Dico G, Semilia F, Milioto S, Parisi F, Cavallaro G, Inguì G, Makaremi M, Pasbakhsh P, Lazzara G, Microemulsion Encapsulated into Halloysite Nanotubes and their Applications for Cleaning of a Marble Surface Applied Sciences (2018) 8(9):1455. https://doi.org/10.3390/app8091455
[18] Stulik D, Dorge V, Miller D, Khanjian H, Institute GC, Carlson J, Khandekar N, Wolbers R, Petersen WC. Solvent Gels for the Cleaning of Works of Art: The Residue Question. Getty Publications; 2004.
[19] Gulotta D, Saviello D, Gherardi F, Toniolo L, Anzani M, Rabbolini A, Goidanich S, Setup of a sustainable indoor cleaning methodology for the sculpted stone surfaces of the Duomo of Milan Herit Sci (2014) 2(1):6. https://doi.org/10.1186/2050-7445-2-6
[20] Mastrangelo R, Montis C, Bonelli N, Tempesti P, Baglioni P, Surface cleaning of artworks: structure and dynamics of nanostructured fluids confined in polymeric hydrogel networks PCCP (2017) 19(35):23762-23772. https://doi.org/10.1039/C7CP02662E
[21] Carretti E, Dei L, Gels as Cleaning Agents in Cultural Heritage Conservation. In: Weiss RG, Terech P, editors. Molecular Gels: Materials with Self-Assembled Fibrillar Networks. Dordrecht, Springer Netherlands, 2006, 929-938. https://doi.org/10.1007/1-4020-3689-2_28
[22] Bonini M, Lenz S, Giorgi R, Baglioni P, Nanomagnetic Sponges for the Cleaning of Works of Art Langmuir (2007) 23(17):8681-8685. https://doi.org/10.1021/la701292d
[23] Domingues JA, Bonelli N, Giorgi R, Fratini E, Gorel F, Baglioni P, Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artifacts Langmuir (2013) 29(8):2746-2755. https://doi.org/10.1021/la3048664
[24] Riedo C, Caldera F, Poli T, Chiantore O, Poly(vinylalcohol)-borate hydrogels with improved features for the cleaning of cultural heritage surfaces Herit Sci (2015) 3(1):23. https://doi.org/10.1186/s40494-015-0053-2
[25] Sun M, Wang J, Zhang H, Zhang B, Fan Z, Su B, Measurement of the reversible rate of conservation materials for ancient murals J Cult Herit (2015) 16(1):49-56. https://doi.org/10.1016/j.culher.2014.01.010
[26] Boccalon E, Nocchetti M, Pica M, Romani A, Sterflinger K, Hydrogels: A 'stepping stone' towards new cleaning strategies for biodeteriorated surfaces J Cult Herit (2021) 47:1-11. https://doi.org/10.1016/j.culher.2020.07.008
[27] Delgado Rodrigues J, Stone Consolidation. Between Science and Practice. In: Gherardi F, Maravelaki PN, editors. Conserving Stone Heritage: Traditional and Innovative Materials and Techniques. Cham, Springer International Publishing, 2022, 101-135. https://doi.org/10.1007/978-3-030-82942-1_4
[28] Tzavellos S, Pesce GL, Wu Y, Henry A, Robson S, Ball RJ, Effectiveness of Nanolime as a Stone Consolidant: A 4-Year Study of Six Common UK Limestones Materials (2019) 12(17):2673. https://doi.org/10.3390/ma12172673
[29] Rodriguez-Navarro C, Elert K, Ševčík R, Amorphous and crystalline calcium carbonate phases during carbonation of nanolimes: implications in heritage conservation CrystEngComm (2016) 18(35):6594-6607. https://doi.org/10.1039/C6CE01202G
[30] Camerini R, Poggi G, Chelazzi D, Ridi F, Giorgi R, Baglioni P, The carbonation kinetics of calcium hydroxide nanoparticles: A Boundary Nucleation and Growth description J Colloid Interface Sci (2019) 547:370-381. https://doi.org/10.1016/j.jcis.2019.03.089
[31] Rodriguez-Navarro C, Ruiz-Agudo E, Nanolimes: From synthesis to application Pure and Applied Chemistry (2018) 90(3):523-550. https://doi.org/10.1515/pac-2017-0506
[32] Chelazzi D, Poggi G, Jaidar Y, Toccafondi N, Giorgi R, Baglioni P, Hydroxide nanoparticles for cultural heritage: Consolidation and protection of wall paintings and carbonate materials Journal of Colloid and Interface Science (2013) 392:42-49. https://doi.org/10.1016/j.jcis.2012.09.069
[33] Michalopoulou A, Maravelaki P-N, Kilikoglou V, Karatasios I, Morphological characterization of water-based nanolime dispersions J Cult Herit (2020) 46:11-20. https://doi.org/10.1016/j.culher.2020.06.005
[34] Zornoza-Indart A, Lopez-Arce P, Leal N, Simão J, Zoghlami K, Consolidation of a Tunisian bioclastic calcarenite: From conventional ethyl silicate products to nanostructured and nanoparticle based consolidants Construction and Building Materials (2016) 116:188-202. https://doi.org/10.1016/j.conbuildmat.2016.04.114
[35] Borsoi G, Lubelli B, van Hees R, Veiga R, Santos Silva A, Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties Construction and Building Materials (2017) 142:385-394. https://doi.org/10.1016/j.conbuildmat.2017.03.097
[36] Taglieri G, Otero J, Daniele V, Gioia G, Macera L, Starinieri V, Charola AE, The biocalcarenite stone of Agrigento (Italy): Preliminary investigations of compatible nanolime treatments Journal of Cultural Heritage (2018) 30:92-99. https://doi.org/10.1016/j.culher.2017.11.003
[37] Daniele V, Taglieri G, Macera L, Rosatelli G, Otero J, Charola AE, Green approach for an eco-compatible consolidation of the Agrigento biocalcarenites surface Construction and Building Materials (2018) 186:1188-1199. https://doi.org/10.1016/j.conbuildmat.2018.08.033
[38] Shekofteh A, Molina E, Rueda-Quero L, Arizzi A, Cultrone G, The efficiency of nanolime and dibasic ammonium phosphate in the consolidation of beige limestone from the Pasargadae World Heritage Site Archaeological and Anthropological Sciences (2019) 11(9):5065-5080. https://doi.org/10.1007/s12520-019-00863-y
[39] Gherardi F, Otero J, Blakeley R, Colston B, Application of Nanolimes for the Consolidation of Limestone from the Medieval Bishop's Palace, Lincoln, UK Stud Conserv (2020) 65(sup1):P90-P97. https://doi.org/10.1080/00393630.2020.1752436
[40] Badreddine D, Beck K, Brunetaud X, Chaaba A, Al-Mukhtar M, Nanolime consolidation of the main building stone of the archaeological site of Volubilis (Morocco) J Cult Herit (2020) 43:98-107. https://doi.org/10.1016/j.culher.2019.12.006
[41] Pesce C, Moretto LM, Orsega EF, Pesce GL, Corradi M, Weber J, Effectiveness and Compatibility of a Novel Sustainable Method for Stone Consolidation Based on Di-Ammonium Phosphate and Calcium-Based Nanomaterials Materials (2019) 12(18):3025. https://doi.org/10.3390/ma12183025
[42] Delgado Rodrigues J, Ferreira Pinto AP, Nogueira R, Gomes A, Consolidation of lime mortars with ethyl silicate, nanolime and barium hydroxide. Effectiveness assessment with microdrilling data Journal of Cultural Heritage (2018) 29:43-53. https://doi.org/10.1016/j.culher.2017.07.006
[43] Otero J, Starinieri V, Charola AE, Nanolime for the consolidation of lime mortars: A comparison of three available products Construction and Building Materials (2018) 181:394-407. https://doi.org/10.1016/j.conbuildmat.2018.06.055
[44] Taglieri G, Daniele V, Macera L, Mignemi A, Innovative and green nanolime treatment tailored to consolidate the original mortar of the façade of a medieval building in L'aquila (Italy) Construction and Building Materials (2019) 221:643-650. https://doi.org/10.1016/j.conbuildmat.2019.06.110
[45] Masi G, Sassoni E, Air lime mortar consolidation by nanolimes and ammonium phosphate: Compatibility, effectiveness and durability

Constr Build Mater (2021) 299:123999. https://doi.org/10.1016/j.conbuildmat.2021.123999
[46] Natali I, Saladino ML, Andriulo F, Chillura Martino D, Caponetti E, Carretti E, Dei L, Consolidation and protection by nanolime: Recent advances for the conservation of the graffiti, Carceri dello Steri Palermo and of the 18th century lunettes, SS. Giuda e Simone Cloister, Corniola (Empoli) Journal of Cultural Heritage (2014) 15(2):151-158. https://doi.org/10.1016/j.culher.2013.03.002
[47] Otero J, Starinieri V, Charola AE, Influence of substrate pore structure and nanolime particle size on the effectiveness of nanolime treatments Construction and Building Materials (2019) 209:701-708. https://doi.org/10.1016/j.conbuildmat.2019.03.130
[48] Matteini M, Inorganic treatments for the consolidation and protection of stone artefacts Conservation Science in Cultural Heritage (2008) 8:13-27.
[49] Sassoni E, Hydroxyapatite and Other Calcium Phosphates for the Conservation of Cultural Heritage: A Review Materials (2018) 11(4):557. https://doi.org/10.3390/ma11040557
[50] Sassoni E, Franzoni E, Pigino B, Scherer GW, Naidu S, Consolidation of calcareous and siliceous sandstones by hydroxyapatite: Comparison with a TEOS-based consolidant J Cult Herit (2013) 14(3, Supplement):e103-e108. https://doi.org/10.1016/j.culher.2012.11.029
[51] Sassoni E, Franzoni E, Sugaring marble in the Monumental Cemetery in Bologna (Italy): characterization of naturally and artificially weathered samples and first results of consolidation by hydroxyapatite Appl Phys A (2014):1-14. https://doi.org/10.1007/s00339-014-8629-3
[52] Franzoni E, Sassoni E, Graziani G, Brushing, poultice or immersion? The role of the application technique on the performance of a novel hydroxyapatite-based consolidating treatment for limestone J Cult Herit (2015) 16(2):173-184. https://doi.org/10.1016/j.culher.2014.05.009
[53] Graziani G, Sassoni E, Franzoni E, Consolidation of porous carbonate stones by an innovative phosphate treatment: mechanical strengthening and physical-microstructural compatibility in comparison with TEOS-based treatments Herit Sci (2015) 3(1):1. https://doi.org/10.1186/s40494-014-0031-0
[54] Sassoni E, Graziani G, Franzoni E, Repair of sugaring marble by ammonium phosphate: Comparison with ethyl silicate and ammonium oxalate and pilot application to historic artifact Mater Des (2015) 88:1145-1157. https://doi.org/10.1016/j.matdes.2015.09.101
[55] Sassoni E, Ugolotti G, Pagani M, Nanolime, nanosilica or ammonium phosphate? Laboratory and field study on consolidation of a byzantine marble sarcophagus Constr Build Mater (2020) 262:120784. https://doi.org/10.1016/j.conbuildmat.2020.120784
[56] Ma X, Balonis M, Pasco H, Toumazou M, Counts D, Kakoulli I, Evaluation of hydroxyapatite effects for the consolidation of a Hellenistic-Roman rock-cut chamber tomb at Athienou-Malloura in Cyprus Constr Build Mater (2017) 150:333-344. https://doi.org/10.1016/j.conbuildmat.2017.06.012
[57] Sassoni E, Delhomme C, Forst S, Graziani G, Hénin J, Masi G, Palazzo A, Rolland O, Vergès-Belmin V, Phosphate treatments for stone conservation: 3-year field study in the Royal Palace of Versailles (France) Mater Struct (2021) 54(4):140. https://doi.org/10.1617/s11527-021-01717-7
[58] Miliani C, Velo-Simpson ML, Scherer GW, Particle-modified consolidants: A study on the effect of particles on sol-gel properties and consolidation effectiveness J Cult Herit (2007) 8(1):1-6. https://doi.org/10.1016/j.culher.2006.10.002
[59] Kim EK, Won J, Do J-y, Kim SD, Kang YS, Effects of silica nanoparticle and GPTMS addition on TEOS-based stone consolidants J Cult Herit (2009) 10(2):214-221. https://doi.org/10.1016/j.culher.2008.07.008
[60] Ksinopoulou E, Bakolas A, Moropoulou A, Modifying Si-based consolidants through the addition of colloidal nano-particles Applied Physics A (2016) 122(4):267. https://doi.org/10.1007/s00339-016-9772-9
[61] Facio DS, Ordoñez JA, Gil MLA, Carrascosa LAM, Mosquera MJ, New Consolidant-Hydrophobic Treatment by Combining SiO2 Composite and Fluorinated Alkoxysilane: Application on Decayed Biocalcareous Stone from an 18th Century Cathedral Coatings (2018) 8(5):170. https://doi.org/10.3390/coatings8050170
[62] Ban M, Mascha E, Weber J, Rohatsch A, Delgado Rodrigues J, Efficiency and Compatibility of Selected Alkoxysilanes on Porous Carbonate and Silicate Stones Materials (2019) 12(1):156. https://doi.org/10.3390/ma12010156
[63] Maravelaki P, Verganelaki A, A Hybrid Consolidant of Nano-Hydroxyapatite and Silica Inspired from Patinas for Stone Conservation. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Cham, Springer International Publishing, 2018, 79-95. https://doi.org/10.1007/978-3-319-72260-3_4
[64] Rodrigues A, Sena da Fonseca B, Ferreira Pinto AP, Piçarra S, Montemor MdF, TEOS Nanocomposites for the Consolidation of Carbonate Stone: The Effect of Nano-HAp and Nano-SiO2 Modifiers Materials (2022) 15(3):981. https://doi.org/10.3390/ma15030981
[65] Verganelaki A, Kilikoglou V, Karatasios I, Maravelaki-Kalaitzaki P, A biomimetic approach to strengthen and protect construction materials with a novel calcium-oxalate-silica nanocomposite Construction and Building Materials (2014) 62(Supplement C):8-17. https://doi.org/10.1016/j.conbuildmat.2014.01.079
[66] Verganelaki A, Kapridaki C, Maravelaki-Kalaitzaki P, Modified Tetraethoxysilane with Nanocalcium Oxalate in One-Pot Synthesis for Protection of Building Materials Ind Eng Chem Res (2015) 54(29):7195-7206. https://doi.org/10.1021/acs.iecr.5b00247
[67] Maravelaki P-N, Kapetanaki K, Stefanakis D, TEOS-PDMS-Calcium Oxalate Hydrophobic Nanocomposite for Protection and Stone Consolidation Heritage (2021) 4(4):4068-4075. https://doi.org/10.3390/heritage4040224
[68] Falchi L, Balliana E, Izzo FC, Agostinetto L, Zendri E, Distribution of nanosilica dispersions in Lecce stone Sciences at Ca'Foscari (2013) (1| 2013).
[69] Zornoza-Indart A, Lopez-Arce P, Silica nanoparticles (SiO2): Influence of relative humidity in stone consolidation Journal of Cultural Heritage (2016) 18(Supplement C):258-270. https://doi.org/10.1016/j.culher.2015.06.002
[70] Zornoza-Indart A, Lopez-Arce P, Zoghlami K, Leal N, Simão J, Marine Aerosol Weathering of Mediterranean Calcarenite Stone: Durability of Ethyl Silicate, Nano Ca(OH)2, Nano SiO2, and Nanostructured Consolidating Products Stud Conserv (2019) 64(2):73-89. https://doi.org/10.1080/00393630.2018.1477654
[71] Vasanelli E, Calia A, Masieri M, Baldi G, Stone consolidation with SiO2 nanoparticles: Effects on a high porosity limestone Constr Build Mater (2019) 219:154-163. https://doi.org/10.1016/j.conbuildmat.2019.05.169
[72] Quagliarini E, Lenci S, The influence of natural stabilizers and natural fibres on the mechanical properties of ancient Roman adobe bricks J Cult Herit (2010) 11(3):309-314. https://doi.org/10.1016/j.culher.2009.11.012
[73] Costa C, Cerqueira Â, Rocha F, Velosa A, The sustainability of adobe construction: past to future Int J Archit Herit (2019) 13(5):639-647. https://doi.org/10.1080/15583058.2018.1459954
[74] Elert K, Pardo ES, Rodriguez-Navarro C, Alkaline activation as an alternative method for the consolidation of earthen architecture J Cult Herit (2015) 16(4):461-469. https://doi.org/10.1016/j.culher.2014.09.012
[75] Michalopoulou A, Maravelaki N-P, Stefanis N-A, Theoulakis P, Andreou S, Kilikoglou V, Karatasios I, Evaluation of nanolime dispersions for the protection of archaeological clay-based building materials Mediterr Archaeol Archaeom (2020) 20(3):221-242.
[76] Camerini R, Chelazzi D, Giorgi R, Baglioni P, Hybrid nano-composites for the consolidation of earthen masonry J Colloid Interface Sci (2019) 539:504-515. https://doi.org/10.1016/j.jcis.2018.12.082
[77] Karapanagiotis I, Manoudis PN, Savva A, Panayiotou C, Superhydrophobic polymer-particle composite films produced using various particle sizes Surf Interface Anal (2012) 44(7):870-875. https://doi.org/10.1002/sia.4930
[78] Facio DS, Mosquera MJ, Simple Strategy for Producing Superhydrophobic Nanocomposite Coatings In Situ on a Building Substrate ACS Appl Mater Inter (2013) 5(15):7517-7526. https://doi.org/10.1021/am401826g
[79] Karapanagiotis I, Hosseini M, Superhydrophobic Coatings for the Protection of Natural Stone. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing, 2018, 1-25. https://doi.org/10.1007/978-3-319-72260-3_1
[80] Gherardi F, Current and Future Trends in Protective Treatments for Stone Heritage. In: Gherardi F, Maravelaki PN, editors. Conserving Stone Heritage: Traditional and Innovative Materials and Techniques. Cham, Springer International Publishing, 2022, 137-176. https://doi.org/10.1007/978-3-030-82942-1_5
[81] Franco-Castillo I, Hierro L, de la Fuente JM, Seral-Ascaso A, Mitchell SG, Perspectives for antimicrobial nanomaterials in cultural heritage

conservation Chem (2021) 7(3):629-669.
https://doi.org/10.1016/j.chempr.2021.01.006
[82] Bellissima F, Bonini M, Giorgi R, Baglioni P, Barresi G, Mastromei G, Perito B, Antibacterial activity of silver nanoparticles grafted on stone surface Environ Sci Pollut Res (2014) 21(23):13278-13286.
https://doi.org/10.1007/s11356-013-2215-7
[83] Becerra J, Mateo M, Ortiz P, Nicolás G, Zaderenko AP, Evaluation of the applicability of nano-biocide treatments on limestones used in cultural heritage J Cult Herit (2019) 38:126-135.
https://doi.org/10.1016/j.culher.2019.02.010
[84] Roveri M, Gherardi F, Goidanich S, Gulotta D, Castelvetro V, Fischer R, Winandy L, Weber J, Toniolo L, Self-cleaning and antifouling nanocomposites for stone protection: properties and performances of stone-nanomaterial systems IOP Conference Series: Materials Science and Engineering (2018) 364:012070.
https://doi.org/10.1088/1757-899X/364/1/012070
[85] Ditaranto N, Loperfido S, van der Werf I, Mangone A, Cioffi N, Sabbatini L, Synthesis and analytical characterisation of copper-based nanocoatings for bioactive stone artworks treatment Anal Bioanal Chem (2011) 399(1):473-481.
https://doi.org/10.1007/s00216-010-4301-8
[86] Gómez-Ortíz N, De la Rosa-García S, González-Gómez W, Soria-Castro M, Quintana P, Oskam G, Ortega-Morales B, Antifungal Coatings Based on Ca(OH)2 Mixed with ZnO/TiO2 Nanomaterials for Protection of Limestone Monuments ACS Appl Mater Inter (2013) 5(5):1556-1565. https://doi.org/10.1021/am302783h
[87] van der Werf I, Ditaranto N, Picca R, Sportelli M, Sabbatini L, Development of a novel conservation treatment of stone monuments with bioactive nanocomposites Herit Sci (2015) 3(1):1-9.
https://doi.org/10.1186/s40494-015-0060-3
[88] uggiero L, Crociani L, Zendri E, El Habra N, Guerriero P, Incorporation of the zosteric sodium salt in silica nanocapsules: synthesis and characterization of new fillers for antifouling coatings Appl Surf Sci (2018) 439:705-711. https://doi.org/10.1016/j.apsusc.2017.12.228
[89] Romano I, Granata G, Poli A, Finore I, Napoli E, Geraci C, Inhibition of bacterial growth on marble stone of 18th century by treatment of nanoencapsulated essential oils Int Biodeterior Biodegrad (2020) 148:104909. https://doi.org/10.1016/j.ibiod.2020.104909
[90] Quagliarini E, Bondioli F, Goffredo GB, Cordoni C, Munafò P, Self-cleaning and de-polluting stone surfaces: TiO2 nanoparticles for limestone Constr Build Mater (2012) 37(0):51-57.
https://doi.org/10.1016/j.conbuildmat.2012.07.006
[91] Gherardi F, Colombo A, D'Arienzo M, Credico B, Goidanich S, Morazzoni F, Simonutti R, Toniolo L, Efficient self-cleaning treatments for built heritage based on highly photo-active and well-dispersible TiO2 nanocrystals Microchem J (2016) 126.
https://doi.org/10.1016/j.microc.2015.11.043
[92] Gherardi F, Goidanich S, Dal Santo V, Toniolo L, Layered Nano-TiO2 Based Treatments for the Maintenance of Natural Stones in Historical Architecture Angew Chem Int Ed (2018) 57(25):7360-7363.
https://doi.org/10.1002/anie.201712752
[93] Cappelletti G, Fermo P, Camiloni M, Smart hybrid coatings for natural stones conservation Prog Org Coat (2015) 78:511-516.
https://doi.org/10.1016/j.porgcoat.2014.05.029
[94] Colangiuli D, Calia A, Bianco N, Novel multifunctional coatings with photocatalytic and hydrophobic properties for the preservation of the stone building heritage Constr Build Mater (2015) 93:189-196.
https://doi.org/10.1016/j.conbuildmat.2015.05.100
[95] Gherardi F, Goidanich S, Toniolo L, Improvements in marble protection by means of innovative photocatalytic nanocomposites Prog Org Coat (2018) 121:13-22.
https://doi.org/10.1016/j.porgcoat.2018.04.010
[96] La Russa MF, Rovella N, Alvarez de Buergo M, Belfiore CM, Pezzino A, Crisci GM, Ruffolo SA, Nano-TiO2 coatings for cultural heritage protection: The role of the binder on hydrophobic and self-cleaning efficacy Prog Org Coat (2016) 91:1-8.
https://doi.org/10.1016/j.porgcoat.2015.11.011
[97] Gherardi F, Roveri M, Goidanich S, Toniolo L, Photocatalytic Nanocomposites for the Protection of European Architectural Heritage Materials (2018) 11(1):65.
https://doi.org/10.3390/ma11010065
[98] Pinho L, Mosquera MJ, Titania-silica nanocomposite photocatalysts with application in stone self-cleaning J Phys Chem C (2011) 115.
https://doi.org/10.1021/jp2074623
[99] Kapridaki C, Maravelaki-Kalaitzaki P, TiO2-SiO2-PDMS nano-composite hydrophobic coating with self-cleaning properties for marble protection Prog Org Coat (2013) 76(2-3):400-410.
https://doi.org/10.1016/j.porgcoat.2012.10.006
[100] Kapridaki C, Pinho L, Mosquera MJ, Maravelaki-Kalaitzaki P, Producing photoactive, transparent and hydrophobic SiO2-crystalline TiO2 nanocomposites at ambient conditions with application as self-cleaning coatings Applied Catalysis B: Environmental (2014) 156:416-427. https://doi.org/10.1016/j.apcatb.2014.03.042
[101] Toniolo L, Gherardi F, The protection of marble surfaces: the challenge to develop suitable nanostructured treatments. In: Hosseini M, Karapanagiotis I, editors. Advanced Materials for the Conservation of Stone. Springer International Publishing, 2018, 57-78. https://doi.org/10.1007/978-3-319-72260-3_3
[102] Sassoni E, D'Amen E, Roveri N, Scherer GW, Franzoni E, Durable Self-Cleaning Coatings for Architectural Surfaces by Incorporation of TiO_2 Nano-Particles into Hydroxyapatite Films Materials (Basel, Switzerland) (2018) 11(2):177. https://doi.org/10.3390/ma11020177
[103] Munafò P, Quagliarini E, Goffredo GB, Bondioli F, Licciulli A, Durability of nano-engineered TiO2 self-cleaning treatments on limestone Constr Build Mater (2014) 65(0):218-231.
https://doi.org/10.1016/j.conbuildmat.2014.04.112
[104] Calia A, Lettieri M, Masieri M, Durability assessment of nanostructured TiO2 coatings applied on limestones to enhance building surface with self-cleaning ability Build Environ (2016) 110:1-10. https://doi.org/10.1016/j.buildenv.2016.09.030
[105] Carmona-Quiroga PM, Martínez-Ramírez S, Viles HA, Efficiency and durability of a self-cleaning coating on concrete and stones under both natural and artificial ageing trials Appl Surf Sci (2018) 433:312-320. https://doi.org/10.1016/j.apsusc.2017.10.052
[106] Roveri M, Goidanich S, Toniolo L, Artificial Ageing of Photocatalytic Nanocomposites for the Protection of Natural Stones Coatings (2020) 10(8):729. https://doi.org/10.3390/coatings10080729
[107] Colangiuli D, Lettieri M, Masieri M, Calia A, Field study in an urban environment of simultaneous self-cleaning and hydrophobic nanosized TiO2-based coatings on stone for the protection of building surface Sci Total Environ (2019) 650:2919-2930.
https://doi.org/10.1016/j.scitotenv.2018.10.044
[108] Becherini F, Pastorelli G, Valotto G, Gambirasi A, Bianchin S, Favaro M, Effects of protective treatments on particle deposition and colour variation in stone surfaces exposed to an urban environment Prog Org Coat (2017) 112:75-85.
https://doi.org/10.1016/j.porgcoat.2017.06.029
[109] Gherardi F, Gulotta D, Goidanich S, Colombo A, Toniolo L, On-site monitoring of the performance of innovative treatments for marble conservation in architectural heritage Herit Sci (2017) 5(1):4.
https://doi.org/10.1186/s40494-017-0118-5