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Headline
Conserving the built heritage with nanomaterials

Standfirst
***Giovanni Pesce ProfGrad** and **Cecilia Pesce** at Northumbria University, UK, discuss the evolving role of nanomaterials in building conservation.

*Bio: Giovanni Pesce is Senior Lecturer at Northumbria University and a member of the IOM3 Cementitious Materials Group.

Cecilia Pesce is a PhD student in Built Environment at Northumbria University, Newcastle upon Tyne.

Body

Since renowned physicist Richard Feynman expounded the potential of miniaturisation in his famous talk, There's plenty of room at the bottom, held at CalTech in 1959, nanomaterials (NMs) have played a fundamental role in various disciplines, ranging from medicine and computer sciences to electrical engineering and automotive. Today, the cultural heritage industry is a further realm where NMs are finding important applications.

Gargoyles protruding from the façades of Gothic cathedrals and decorative plasterworks of medieval architecture are examples of artefacts bearing significant artistic or historic value that is embedded in built heritage. In this field, conservation and restoration treatments are periodically accomplished and products based on NMs have been successfully applied to these purposes. These products, developed over the last few decades, mainly consist of sols of inorganic nanoparticles that are usually brushed, dripped or applied via poultices onto the architectural surfaces. Many of these colloidal suspensions are still in development and are either tailored with new functional modifications for specific uses – or produced through more cost-effective and scalable routes – or show enhanced performances, whereas others are already commercially available and specifically developed for the conservation of cultural heritage. These include the nano-limes Nanorestore and Calosil, and nano-silica NanoEstel and Ludox.

Over the last 20 years, various national and international multi-disciplinary projects have been supported by large grants to promote the development of nanomaterials for the conservation industry. One example of this is the recent €7mln project, Nano-Cathedral, funded by the European Union under Horizon 2020. The project, aimed at developing nanostructured materials for the conservation of stones used in historic buildings, resulted in the formulation of novel nano-composites based on minerals such as hydroxyapatite, zinc oxide, aluminium oxide and calcium carbonate. These materials were tested on a wide variety of stone types, subject to different climatic and environmental conditions and representative of different European areas and styles, thanks to the collaboration between representatives of the institutions managing some of the most iconic European cathedrals, as well as geologists and materials scientists, conservators and industrial partners.

The role of nanoparticles

Within conservation of the built heritage, NMs have various uses with one of the most common being consolidation of original materials which have often degraded to a point where the surface is rich in loose particles. Two of the most common nano-consolidants are nanolime and nanosilica. Products developed for this application penetrate the material's porous network and set inside it, providing some cohesion to loosen fragments and binding the decayed surface layer to the sound underlying substrate. Compared with traditional products, nanostructured consolidants have multiple advantages, such as a deeper penetration of the substrate due to the reduced size of the particles, a stronger adhesion to the pore walls from the higher density of established interfacial interactions between the consolidant and the original material, and the possibility to use a low-viscosity, often non-aqueous, liquid medium with high concentrations of solid phase dispersed therein.

Another important function is the protection of outdoor architectural surfaces from external causes of degradation, such as weathering agents. This category of material are typically spread onto the surface that need to be treated where they form a film that acts as a physical barrier, hindering the access of weathering agents into the stone pores. Nanostructured protectives are usually nano-composites made of film-forming polymers and titanium oxide (TiO_2) nanoparticles, with photocatalytic properties that provide the surfaces with auto-cleaning, antifouling and antibacterial properties.

Calcium-based nanoconsolidants

A well-known example of nanostructured material used in the conservation of the built heritage is nanolime, a suspension of calcium hydroxide nanoparticles (CHNPs) in alcohol used to consolidate carbonate materials, such as limestone and lime-based renders. Traditionally, consolidation of these substrates was carried out using saturated aqueous solutions of calcium hydroxide or cloudy suspensions of lime in water. Stable suspensions of CHNPs started to be developed in the 1970s at the University of Florence, Italy, after the devastating flood that hit the city in 1966 required large-scale restoration work to preserve a number of affected masterpieces.

To support the repair work, nanolime was developed to consolidate frescoes, where the substrate is a porous lime-based mortar, and subsequently has been applied to other materials, such as paper and, more recently, stones. The introduction of the nanostructured particles of calcium hydroxide, besides the advantages previously listed, also improves the carbonation rate due to the high specific surface area of the particles.
Current research focuses on the selection of the synthetic strategy to prepare CHNPs since this matter is crucial for tailoring the characteristics of the final product.

The most common bottom-up approach – preferred over cheaper top-down methods that cannot produce nano-sized particles – entails homogeneous precipitation of CHNPs by mixing aqueous solutions of calcium chloride and sodium hydroxide and subsequent peptisation in alcohol. The crystal size is controlled via selection of various parameters such as temperature and pressure of reaction to maximise the degree of supersaturation of the precipitating solution and hence to promote the formation of crystals nuclei over crystal growth. Through this route, plate-like crystals of 150-400nm in diameter and about 15-40nm in height are produced. Once the right size is reached, peptisation in alcohol blocks the crystal growth and ensures colloidal stability. The preferred carriers in commercial products are usually ethanol or isopropanol, as short-chain alcohols can minimise agglomeration and clustering, and have surface tension and volatility that allow adequate penetration and drying rate.

- Recent years have seen innovative approaches to CHNPs synthesis attempting to overcome the limitations of the current routine procedures, which include a low solid phase yield and the need of washing and purification to remove residual contaminants – steps that inevitably increase time and cost of production. Indicative of its success, a patent for a potentially scalable method to produce stable aqueous CHNPs dispersions at ambient temperature and pressure, based on the use of an ion exchange resin, was recently filed (European patent EP2880101, 2016). The successful application of the product on a lime mortar affected by detachments and pulverisation was reported by University of L'Aquila Professor, Giuliana Taglieri in *Construction and Building Materials* in June 2019.

A further viable route to synthesise stable CHNPs at ambient temperature was suggested in a paper by Complutense University of Madrid, Spain, scientist Sagrario Martinez-Ramirez in the paper, *New approach to nanolime synthesis at ambient temperature,* published in *SN Applied Sciences* in December 2019. In this study, aqueous solutions of sucrose and mannitol raise calcium solubility through formation of complexes and the related CHNPs formation takes place at ambient temperature, producing particles in the size range between 200-250nm.

Silica-based nanoconsolidants

Within the conservation industry, the term nano-silica identifies a variety of products based on aqueous suspensions of nano-sized silica particles of less than 20nm, used for consolidation treatments of natural stones, bricks, terracotta tiles, renders. These products are meant to replace alkoxysilanes, consolidants traditionally applied on silica-based substrates during conservation works. Alkoxysilanes are usually found on the market as solutions of ethyl silicate in white spirit and they set by *in situ* polymerisation through a classical sol-gel process.

Their upgrading to nanostructured products introduces the advantages of a reduced reaction time for silica gel formation and the use of an aqueous dispersion in place of a volatile organic solvent – a change with significant implications for the health and safety of the conservators, in particular when dealing with the treatment of large surfaces. The synthesis of colloidal nano-sized silica, though, is not a new process since it is still based on the Stöber process, developed in the 1960s. This is a two-step process that entails first the hydrolysis of the alkoxysilane precursor and secondly condensation of the silanol units catalysed by ammonia in a water/alcohol co-solution. One of the main disadvantages of the nano-particles produced using this method is the cracking that is easily induced to the treated stone during curing, due to the stress generated by the polymerisation.

A novel silica-based nanomaterial recently developed and already commercially available under Spanish patent No. P201200152 involves as the starting sol a silica oligomer and a surfactant, which allows reducing the stress development during curing and catalyses the sol-gel reaction. In February 2015, University of Vigo, Spain, Dr Ivan De Rosario reported on trials of the product – a sol of alkoxysilane and n-octylamine in aqueous solution named UCA-2o – which were carried out on the south façade of the Church of Santa Maria del Campo in A Coruña, Spain. The building has a fine-grained granite that had been affected by scaling and granular disintegration, and the NM proved successful in this treatment.

Protective nanocomposites

Deterioration of stone surfaces by weathering agents is relevant in urban and rural environments, whereas the deterioration due to agents of anthropic origin, for instance acid rain, is more relevant in urban areas, usually characterised by a high concentration of historic buildings. Similarly, bio-deterioration is an important issue that affects outdoor surfaces of historic buildings, especially in environments where specific levels of relative humidity, temperature and sunlight exposure create favourable conditions for the growth of microorganisms. A modern method to protect the architectural surfaces from deteriorating agents of anthropic origin and organic depositions is the use of hybrid coatings containing TiO_2 nanoparticles (NPs).

The well-known photocatalytic properties of TiO_2 NPs, in fact, are exploited in the conservation of the built heritage to produce protective coatings able to break up organic matter depositions upon exposure to UV radiation. The effectiveness of the manifold functions of nano-TiO_2 for the protection of stone surfaces has been investigated in terms of biocide and self-cleaning effects by various researchers.

In a 2012 study by University of Calabria, Italy, Associate Professor, Mauro La Russa, the biocide properties of nano-TiO_2 dispersed in an acrylic polymer aqueous dispersion were tested in laboratory trials on specimens of marble and calcareous stone that after treatment were inoculated with strains of the fungus *Aspergillus niger*. The coating showed to be effective at halving the number of these colonies. The self-cleaning property was also evaluated by measuring the colour variations over a period of time after application of methylene blue, where it was observed that the self-cleaning effect lasts longer on coarse-grained lithotypes due to a deeper penetration of the TiO_2 NPs into the pores, when compared with a compact stones, such as Carrara marble.

The main limitation in the application of nano-TiO_2 on architectural surfaces is, however, the induced super-hydrophilicity of the treated surface, consequence of the photocatalytic activity of the nano-structured mineral. Generally, a protective coating applied on outdoor architectural surfaces should have hydrophobic properties in order to reduce the detrimental consequences of water, such as the circulation of soluble salts and bio colonisation. The super-hydrophilicity of TiO_2 can be reduced by dispersing the TiO_2 NPs in acrylic or polyurethane polymer emulsions, however, this characteristic is still a matter of debate among the scientific community and the conservators. The super-hydrophilicity, in fact, may have some advantages as it promotes the formation of a surface film of water, which hinders soil adhesion and does not enhance water absorption into the stone substrate.

A risk for humans and the environment?

Currently, the main concern for the NMs used in conservation of built heritage lays in the possible risks and long-term implications for human health and the environment, but this is still a matter of debate following initial steps taken in 2008, when the European Commission adopted the *Code of conduct for responsible research in the field of nanotechnology*. However, most of the NMs used in the conservation of historic buildings are dispersed in liquid and subsequently deposited inside the material’s pores. Hence, human exposure and substance release in the environment is limited.

A deliverable of the Nano-cathedral project concluded that, among the different inorganic NPs that were investigated, only the use of ZnO might involve some risks, as evidenced by previous systematic and comparative works. Unfortunately, systematic studies can be found only for TiO_2, Ag and ZnO NPs, whereas for other compounds, further research is needed. Despite the clear need for further studies, especially *in vivo* animal studies, however, health and environmental risks related to the use of all tested NMs are assessed to be low.

Figure 1: One of the finely carved stones decorating the external walls at Salisbury Cathedral that was treated with nanolime

Figure 2: Testing nanomaterials for building conservation in one of the international multi-disciplinary research projects

Figure 3: AFM images of a nanocrystal of nano-lime. Top view (top) shows the typical hexagonal shape of calcium hydroxide crystals whereas the cross sections (bottom) show the flat profile of the top face

Figure 4: TEM image of various nano-lime crystals showing the typical hexagonal shape of calcium hydroxide