



Improvements in marble protection by means of innovative photocatalytic nanocomposites



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ABSTRACT

The application of photocatalytic and self-cleaning nanomaterials in the field of architectural heritage is an encouraging strategy for stone conservation and particularly for marble elements. In the present research, self-cleaning nanocomposites were set-up by mixing water dispersions of TiO₂ nanoparticles in commercial protective treatments based on organosiloxanes, fluoropolyethers and functionalized SiO₂. The pure anatase phase nanoparticles used for their preparation are photoactive under solar light, in addition to UV radiation, due to their benzyl surface capping resulting in an increase of their efficiency in the degradation of pollutants. The nanomaterials applied on Carrara marble specimens show better performance in terms of surface colour compatibility and water repellency compared to traditional protective products. Actually, the introduction of nano-TiO₂ plays a role in the increase of the surface roughness, with a consequent reduction of the surface wettability.

1. Introduction

Two main classes of protective treatments have been used in the field of stone conservation aiming at reducing the impact of pollution on the rapid degradation of limestones and marbles since the mid-20th century. The first wide class is the one of synthetic polymeric materials (acrylic, partially fluorinated and perfluoropolymers, alkyl silicon products) which are able to turn the partial hydrophilic properties of the stone into water-repellent surfaces and the second one includes low molecular weight inorganic products (silica sols and ammonium oxalate) [1–3]. Many studies proved that an “all-purpose” protective product suitable for all lithotypes does not exist as far as different factors influence the performance of a water repellent treatment: the chemical nature and formulation of the product (composition, solvent, concentration, water-emulsion, additives, catalyst, etc.), the mineralogical features, morphology, open porosity and state of conservation of the stone substrate, the application method (by brush, by spray, by absorption) and therefore the penetration depth of the treatment [1]. To find an effective strategy for the protection of low porosity stones, such as marbles, is particularly difficult, due to the poor penetration of the treatments into the substrate, which prevents the good coverage and adhesion of the products to the crystal grains, compromising their effectiveness. In addition, the accumulation of the product on the surface makes it more prone to chemical, thermal, photochemical and mechanical stress, with consequent faster deterioration [2].

Therefore, in the last decade, the scientific research has been devoted to developing innovative surface treatments for the protection of exterior stone surfaces of historic buildings. A diffused strategy is the introduction of nanoparticles inside a polymeric matrix, in order to increase the surface roughness without changing the main characteristics of the material, such as permeability and transparency, and the substrate morphology. When the treated surfaces are exposed to rainfall and humidity, water spherical droplets can easily absorb dust and dirt and roll away, giving rise to the so called “self-cleaning” behaviour [4]. The increase of the water-repellency of the surface is due to the formation of micro-nano binary structures which enhance the surface roughness and reduce the real contact between the liquid water and the stone material. As a result, hydrophobic or super-hydrophobic (static contact angle with water > 150°) surfaces are obtained. Polymeric water dispersions have been modified by adding different nanoparticles (SiO₂, SnO₂, Al₂O₃, TiO₂) with the aim of developing surface coatings for natural stones [5–9].

Since 1990s titania nanoparticles have been used, thanks to their photocatalytic properties, in addition to traditional building materials such as concrete, cement mortar, ceramic tiles, paints, glass and PVC fabric [10–12]. In recent years, nano-TiO₂ has been also tested in the field of cultural heritage conservation, in particular for the development of photocatalytic and antifouling treatments for stone substrates [13]. When irradiated with photons having energy higher than their band-gap, titania nanoparticles are able to oxidize and decompose

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organic and inorganic compounds in contact with their surface, generating non-harmful products that can also be easily removed by rainfall [10,14]. In addition to the photocatalytic activity, some nano-TiO₂ treatments show antifouling properties and are able to prevent biological growth [15–17]. Titania nanoparticles have been used in forms of water or solvent dispersions and applied by brush or by spray directly on the surface of different natural stones (limestones, marble, calcarenite, travertine), making them hydrophilic or superhydrophilic [18–20]. The main limit of these dispersions is that nanoparticles show poor adhesion to stone surfaces and are easily removed by rainfall, or they penetrate into the stone porosity, significantly compromising their photocatalytic activity [21]. A strategy to overcome this issue and avoid the release of nanoparticles in the environment is their introduction in either organic or inorganic matrix [16,21–23]. Different types of TiO₂ nanoparticles have been mixed with polymeric matrix used for the protection of stone surfaces such as alkyl silicon products [8,21,24–28], fluorinated or partially fluorinated [29,30] or acrylic [15,30,31] polymers.

A critical issue in the development of nano-TiO₂ based treatments is their poor photoactivity under solar light irradiation, since TiO₂ based nanomaterials present wide band-gaps, mainly adsorbing ultraviolet photons while solar light only contains a small fraction of ultraviolet photons (about 5%). For this reason, the scientific research aims at improving the photocatalytic efficiency of TiO₂ under solar light irradiation, by means of morphological modifications such as the increase of surface area and porosity, or chemical modifications with incorporation of dopants in the TiO₂ structure to reduce the band-gap and extend the spectral sensitivity from UV to visible light [11,32].

In the present research, the set-up of different organic nanocomposites is proposed, starting from commercial stone protective treatments which were improved by the addition of innovative TiO₂ nanoparticles. The latter are characterized by a surface capping of benzyl alcohol molecules anchored on their surfaces, which make the nanoparticles photoactive even if exposed to solar irradiation, increasing their photoefficiency [33]. In addition, as previously reported, the proposed nanocrystals allow to obtain highly stable dispersions in aqueous systems, without affecting the surface colour of the stone substrate [34]. The laboratory experimental work allowed to assess the effectiveness of nanocomposites as protective and self-cleaning treatments for a low porosity stone substrate such as Carrara marble. This stone is mainly composed of regular small size calcite grains, with an average open porosity ranging from 0.5 to 1.0% and it is, therefore, quite difficult to protect. The pores are arising from the reduced intergranular space, which can be enhanced near the surface by deterioration phenomena [35] and are permeable to aggressive gaseous pollutants and corrosive water solutions, but difficult to cover with water repellent treatments. This study accounts for the challenge to address the critical issues for marble protection.

A thorough comparison between the behaviour of the different treatments before and after the addition of nano-TiO₂, has been carried out and discussed.

2. Materials and methods

2.1. Preparation of TiO₂-based nanocomposites and their application on marble specimens

Nanocomposites were set-up by adding water dispersion of nano-TiO₂ to commercial protective treatments used in the conservation field for stone protection. In particular, transparent water dispersion of TiO₂ nanoparticles (3% by weight, nanoparticles size around 40 nm), synthesized according to the non-aqueous route [36], as reported in previous papers [34,37], were used for the preparation of the nanocomposites. The nanoparticles show photoactivity in the visible spectral range in addition to UV, due to the residual presence of benzyl alcohol group on the surface of the nanoparticles, deriving from the synthesis.

Table 1

Values of average dry matter (g) of products applied by brush on stone specimens with a surface area of about 25 cm².

Treatment	Description	Amount of product (g)
S	Commercial polysiloxane <i>Silo 112</i>	0.06 ± 0.01
Sn16	nanocomposite based on polysiloxane <i>Silo 112</i> with nano-TiO ₂ (16 wt%)	0.12 ± 0.01
Sn28	nanocomposite based on polysiloxane <i>Silo 112</i> with nano-TiO ₂ (28 wt%)	0.14 ± 0.01
Sn44	nanocomposite based on polysiloxane <i>Silo 112</i> with nano-TiO ₂ (44 wt%)	0.14 ± 0.01
F	Commercial fluoropolyethers <i>Fluoline PE</i>	0.08 ± 0.01
Fn16	nanocomposite based on fluoropolyethers <i>Fluoline PE</i> with nano-TiO ₂ (16 wt%)	0.10 ± 0.01
FS	Commercial functionalized SiO ₂ <i>SIOX-5 S</i>	0.02 ± 0.01
Fsn16	nanocomposite based on functionalized SiO ₂ <i>SIOX-5 S</i> with nano-TiO ₂ (16 wt%)	0.09 ± 0.01

The selected commercial products for stone materials are: an aqueous dispersion of organosiloxanes (10% by weight) (*Silo 112*, *CTS srl*, labelled as S), an aqueous dispersion of fluoropolyethers (10% by weight) (*Fluoline PE*, *CTS srl*, labelled as F) and a solution of SiO₂ functionalized by silicon alcoxides in isopropyl alcohol (20% by weight) (*SIOX-5 S*, *Siltea srl*, labelled as FS). S and F [29,38] have been chosen as they are products widely used in the field of stone conservation; FS is a promising inorganic protective treatment obtained by sol-gel process from an Italian spin-off company (*Siltea srl*, Italy).

Nanocomposites were prepared by adding, upon stirring, different amount of water dispersion of nanoparticles to the commercial products as sold, without any further dilution. The obtained composites are reported in Table 1. In particular, adding the nanoparticle (n) dispersion to the polysiloxane-based treatment (*Silo 112*, S), three different emulsions were obtained, labelled Sn16, Sn28 and Sn44, showing the following concentrations of nanoparticles in the polymer by weight: 16%, 28% and 44%, respectively.

For both fluoropolyethers-based (*Fluoline PE*) and functionalized SiO₂-based treatments (*SIOX-5 S*), only one composite was obtained, with a 16% by weight nanoparticle concentration (labelled Fn16 and Fsn16, respectively), since the addition of higher amount of nanoparticles did not grant the preparation of stable composites.

Before the application of the treatments, 50 × 50 × 10 mm and 50 × 50 × 20 mm specimens of fresh Carrara marble were prepared by smoothing their surface with abrasive carborundum paper (Nr. 180), washing with deionized water and drying for 48 h at room temperature until constant weight was achieved. They were finally stored in silica gel desiccator at 55% UR.

The nanocomposites were, then, applied following one single brush application, wetting completely the marble surface (about 25 cm²) with the product. The amount of adsorbed dry matter was measured after drying and the values are reported in Table 1. The variations in the values of average amount of dry matter can be ascribed to differences in the density of the products, and in their ability to homogeneously cover the stone surfaces. Untreated stone specimens (labelled NT) were also tested for comparison.

2.2. Characterization of TiO₂-based nanocomposites and evaluation of their effectiveness applied on stone

To evaluate the morphology of nanoparticles and their distribution in the blends, the nanocomposites were analysed using Transmission Electron Microscopy (TEM, Philips CM200-FEG) operated at 200 kV. The samples for TEM analyses were prepared by depositing 1 drop of the nanoparticles dispersions onto a carbon coated copper grid of 200 mesh.

The nanocomposites were chemically characterized by micro-

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