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**Titel:** Layered nano-TiO<sub>2</sub> based treatments for the maintenance of natural stones in historical architecture

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# Layered nano-TiO<sub>2</sub> based treatments for the maintenance of natural stones in historical architecture

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**Abstract:** Layered treatments of natural stones based on dispersions of experimental nano-TiO<sub>2</sub> and commercial TEOS, showing photocatalytic and self-cleaning properties have been set-up and tested. To enhance nano-TiO<sub>2</sub> efficacy, a surface pre-treatment with tetraethyl orthosilicate has been proposed to avoid the penetration of NPs into the crystalline porous substrates and to improve their adhesion to the stone. Two treatment applications – wet-on-wet and wet-on-dry – have been compared, showing different results. A strong interaction Si-O-Ti has proved to be the key factor for the successful treatment, leaving the bandgap and relevant properties of nano-TiO<sub>2</sub> unaltered. The layered treatments have been tested on a porous calcarenite (Noto stone) and a very compact marble (Carrara marble). The combined SiO<sub>2</sub>-nano-TiO<sub>2</sub> treatments can find application in suitable cases where a surface consolidation is needed, ensuring a depolluting and self-cleaning durable activity.

The growing attention in the use of TiO<sub>2</sub> nanoparticles (NPs) in the development of self-cleaning treatments arises from their specific properties: photocatalysis and superhydrophilicity. Both phenomena are photoinduced and take place simultaneously, leading to the production of superoxide radical anions and hydroxyl radicals and the adsorption of OH groups from water molecules which fill the oxygen vacancies<sup>[1]</sup>. The twofold behavior makes this material capable of degrading organic and inorganic pollutants and the hydrophilic surface allows the easy removal of reaction products by water, preventing the contaminants contact with treated surface. In the field of built heritage conservation the use of TiO<sub>2</sub> NPs represents a preventive strategy for the maintenance of stone surfaces against environmental decay agents<sup>[2]</sup>. Self-cleaning products have been set-up according to 2 routes considering the occurring surface wettability changes. Superhydrophilic or hydrophilic surfaces are obtained by nano-TiO<sub>2</sub> (nTiO<sub>2</sub>) dispersions in different solvents (e.g., water, alcohol, ethylene glycol)<sup>[3]</sup>. Superhydrophobic and hydrophobic properties are exhibited by stone treated with nanocomposites that combine nano-TiO<sub>2</sub> with polymers (e.g., alkyl-silane, alkyl-aryl polysiloxane, fluorinated and acrylic copolymers)<sup>[4]</sup> or with hybrid organic and inorganic compounds<sup>[5]</sup>. Both synthesis routes display limitations in terms of lifespan and durability: nano-TiO<sub>2</sub> dispersions show poor adhesion and chemical affinity with the substrate, as they can be easily removed by rainfall and tend to penetrate into the pores, with a consequent dramatic decrease of their photoefficiency<sup>[6]</sup>; in nanocomposites, instead, the polymeric matrix can be compromised by the photocatalytic activity of the embedded NPs<sup>[7]</sup>.

Objective of a previous research was the evaluation of water and ethylene glycol dispersions of innovative nano-TiO<sub>2</sub> applied low and high porosity stones<sup>[3e]</sup>. The anatase NPs are characterized by benzyl alcohol capping agent, able to extend the photocatalytic activity under solar light irradiation due to the formation of defects within energy bandgap. Compared to some renowned commercial NPs, these dispersions exhibit improvements: no aggregation, higher stability and transparency in aqueous systems, no alteration of colour and texture of the stone substrate and higher photoactivity. However, field exposure monitoring of treated stone specimens (marble and calcarenite) in urban polluted environment, pointed out that the innovative NPs don't show satisfactory oxidizing and self-cleaning properties<sup>[7]</sup>.

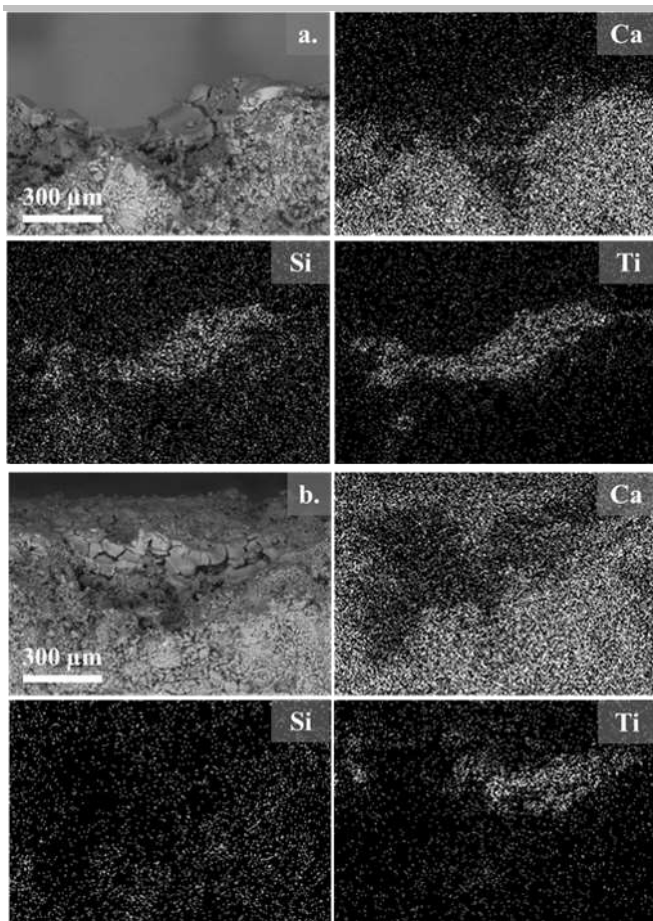
The original aspect of this work regards the set-up of layered nano-TiO<sub>2</sub> dispersions (SiO<sub>2</sub>-nTiO<sub>2</sub>) combined with a surface consolidation material (tetraethyl orthosilicate, TEOS) to stabilize the NPs on the surface and avoid the penetration into the pores, without affecting the stone hydrophilic character. Water dispersion of nTiO<sub>2</sub> was brushed on 2 lithotypes (Noto stone and Carrara marble) by following two different procedures: a) application of nTiO<sub>2</sub> dispersion on wet surface pre-treated with TEOS (wet-on-wet technique, labeled as W-T75/T100-nTiO<sub>2</sub>); b) application of nTiO<sub>2</sub> dispersion on dried surface, after the complete hydrolysis and gelation of the silica gel (wet-on-dry technique, labeled as D-T75/T100-nTiO<sub>2</sub>).

The study of the morphology and penetration of the treatments applied on stone specimens was performed by ESEM-EDX analyses. For both lithotypes, the treatments change the morphology of the stone surface, covering the crystals with a rather thick layer of amorphous silica structured in small plaques. The products applied following the wet-on-wet technique (W-T75-nTiO<sub>2</sub> and W-T100-nTiO<sub>2</sub>) are more homogeneously distributed on the stone surface compared to D-T75-nTiO<sub>2</sub> and D-T100-nTiO<sub>2</sub>, as it can be easily inferred by the main elements (Ca, Si and Ti) maps (Figure S1-S5). In addition, by observing the cross-sections of Noto stone treated with W-T75-nTiO<sub>2</sub> and W-T100-nTiO<sub>2</sub>, the signals of silica gel (Si) and the nano-TiO<sub>2</sub> (Ti) overlay, indicating that the NPs are inserted in the silica network (Figure 1a). This demonstrates the chemical affinity between the nTiO<sub>2</sub> and both solvent-based and solventless TEOS. The combined SiO<sub>2</sub>-nano TiO<sub>2</sub> layer lays onto the stone surface and reaches a penetration depth of few  $\mu\text{m}$ . These evidences prove that the wet-on-wet application of nTiO<sub>2</sub> after TEOS by brush prevents the penetration of the material into the highly porous calcarenite, anchoring the NPs onto the surface. On the contrary, in the sections of Noto stone treated with D-T75-nTiO<sub>2</sub> and D-T100-nTiO<sub>2</sub>, TEOS and nTiO<sub>2</sub> have different penetration depths into the substrate: the consolidant diffuses in the porous structure while the NPs are laying on the surface (Figure 1b). Although less evident because of the lower thickness of the treatment layer, the same behavior can be observed on Carrara marble samples (Figure 2). On Noto stone probably the higher surface roughness and porosity grant the formation of a thicker treatment layer compared to the marble

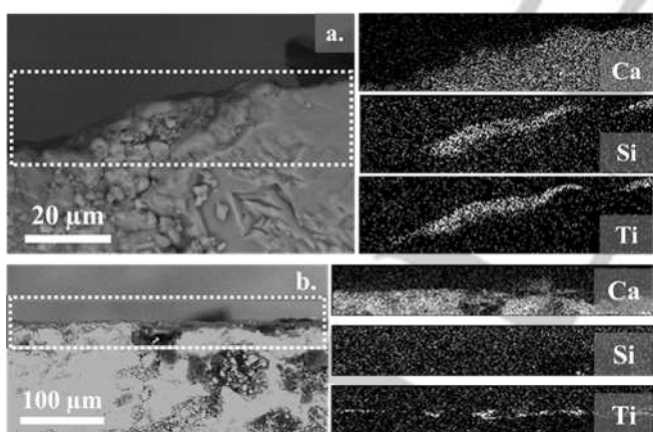
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**Figure 1.** ESEM-EDX images of Noto stone section treated with: a) W-T75-nTiO<sub>2</sub>; b) D-T75-nTiO<sub>2</sub> and Ca, Si and Ti maps of distribution.



**Figure 2.** ESEM-EDX images of Noto stone section treated with: a) W-T75-nTiO<sub>2</sub>; b) D-T75-nTiO<sub>2</sub> and Ca, Si and Ti maps of distribution.

The microscopic changes in the stone morphology are not mirrored by significant alterations of the surface colour (colour difference  $\Delta E^*$  about 3.60 for Noto stone and about 2.60 for Carrara marble) (Table S2), proving the high aesthetic colour compatibility of the layered treatments on both substrates.

Static contact angle measurements were carried out to measure the change in surface wettability induced by treatments, since n-TiO<sub>2</sub> is able to confer superhydrophilic properties to the surface [8]. On Carrara marble, all the nanostructured materials (W-T75-

nTiO<sub>2</sub>, D-T75-nTiO<sub>2</sub>, W-T100-nTiO<sub>2</sub> and D-T75-nTiO<sub>2</sub>) exhibit an increase of the surface wettability compared to the thermally aged untreated specimens and those with the consolidant (T75 and T100) (Table S4). These results evidence the treatments ability to display a self-cleaning behaviour in outdoor conditions (upon solar light irradiation).

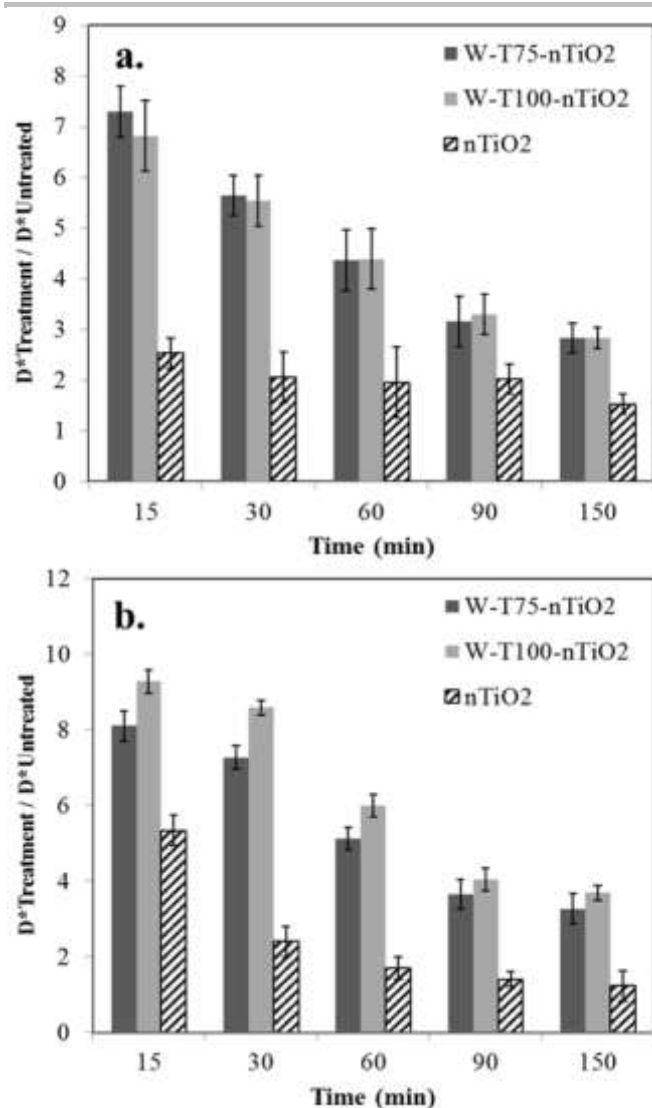
Water absorption by capillarity tests point out that the wettability increase does not result in higher amount of absorbed water (Table S3 and S4). For both stone substrates, a modest reduction of capillary absorption is observed (about 10% for Noto stone; 30% for Carrara marble) that is due to the treatment with TEOS and not affected by the nTiO<sub>2</sub> presence. Actually, comparable values of relative capillary index ( $CI_{rel}$ ) were obtained by both T75 and T100 consolidant and by W-T75-nTiO<sub>2</sub>, D-T75-nTiO<sub>2</sub>, W-T100-nTiO<sub>2</sub> and D-T75-nTiO<sub>2</sub> (Table S3 and S4). Although TEOS treatments usually exhibit hydrophilic properties [9], the reduction in water absorption of the treated marble specimens can be explained by a changing in the pore size distribution.

The assessment of the photocatalytic activity of the treated stone surfaces was carried out by evaluating the discoloration of rhodamine B colorant ( $D^*$  %) after pre-fixed intervals of exposition to solar light irradiation (xenon lamp). The curves of  $D^*$  values of both lithotypes indicate that the treated surfaces (W-T75-nTiO<sub>2</sub>, D-T75-nTiO<sub>2</sub>, W-T100-nTiO<sub>2</sub> and D-T75-nTiO<sub>2</sub>) show significantly higher discoloration rate compared to the untreated specimens (Figure S6). Moreover, two different trends associated with the application methodology - wet-on-wet and wet-on-dry - can be noticed. For both lithotypes, the best performances were achieved by specimens with W-T75-nTiO<sub>2</sub> and W-T100-nTiO<sub>2</sub>, which reach  $D^*$  values of 80% in Noto stone and about 70% in Carrara marble respectively at the end of the test (Figure S6). The poorer performances of D-T75-nTiO<sub>2</sub> and D-T100-nTiO<sub>2</sub> treatments, should be connected to the not homogenous distribution of nTiO<sub>2</sub> on the stone surface, as observed by ESEM-EDX (Figure S2-S5). NPs homogeneously dispersed in the silica network, obtained by wet-on-wet treatment, show a higher photocatalytic activity. By comparing the data of the ratio between  $D^*$  values of Noto stone and Carrara marble treated with wet-on-wet SiO<sub>2</sub>-nTiO<sub>2</sub> treatments (W-T75-nTiO<sub>2</sub> and W-T100-nTiO<sub>2</sub>), water dispersion of nano-TiO<sub>2</sub> 3%wt (nTiO<sub>2</sub>) and the untreated specimen (NT), the highest photoactivity is assessed for those pretreated with TEOS (Figure 3). The higher photocatalytic activity of wet-on-wet SiO<sub>2</sub>-nTiO<sub>2</sub> treatments compared to the simple dispersion of NPs can be ascribed to the favorable distribution of nTiO<sub>2</sub> in the final silica gel, showing a higher amount of NPs on the surface.

In order to better investigate the satisfying performance of wet-on-wet layered treatments compared to both wet-on-dry nTiO<sub>2</sub> dispersions, an evaluation of the possible chemical interactions between silica gel and nTiO<sub>2</sub> was carried out by means of micro-FTIR spectroscopy. The frequency range of interest to study these interactions is reported in Figure 3. In particular, a shift of the peak at 950 cm<sup>-1</sup> in T75 and D-T75-nTiO<sub>2</sub> to lower frequencies (about 910 cm<sup>-1</sup>) can be evidenced in W-T75-nTiO<sub>2</sub>. Bands that lie at around 950 cm<sup>-1</sup> are attributed to Si-OH stretching vibrations whereas bands at 910 cm<sup>-1</sup> can be assigned to the stretching vibrations of Si-O-Ti bonds [5a, 10]. The shift of these peaks evidences that nTiO<sub>2</sub> strongly interact with the silica gel network, modifying the vibration modes of the Si-O when they are applied on wet surfaces pre-treated with TEOS [5a]. The peak shift cannot be observed in the case of the wet-on-dry treatment (D-T75-nTiO<sub>2</sub>), suggesting that the application methodology plays a key role in the exploitation of nTiO<sub>2</sub> properties.

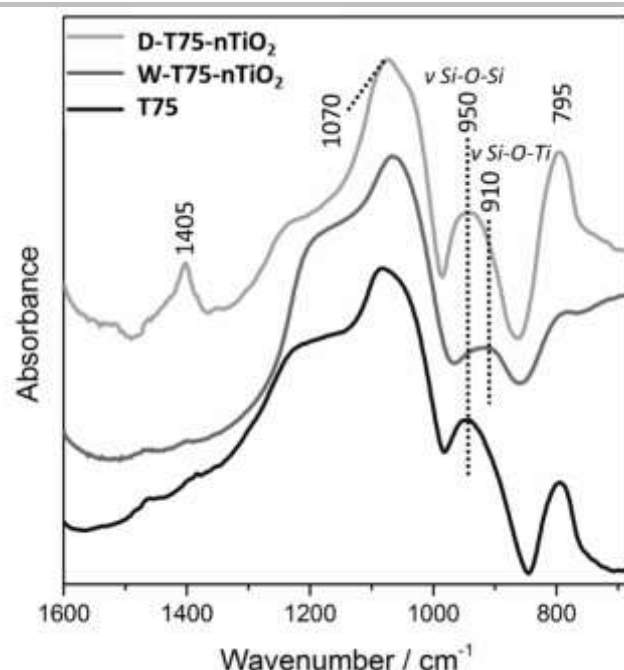


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**Figure 3.** Ratio between the values of stain discoloration  $D^*$  of: a) Noto stone specimens and b) Carrara marble treated with  $\text{SiO}_2$ - $n\text{TiO}_2$  treatments (W-T75- $n\text{TiO}_2$  and W-T100- $n\text{TiO}_2$ ) and water dispersions of nano- $\text{TiO}_2$  (3%) ( $n\text{TiO}_2$ ) and the untreated specimen (Untreated), at different time intervals (min).

Band gap energy values were also evaluated to assess any modification induced by the formation of a combined  $\text{SiO}_2$ - $n\text{TiO}_2$  layer. As reported in Table S6, band gap energy values ranging from 3.65 to 3.73 eV were obtained by both  $n\text{TiO}_2$  and  $\text{SiO}_2$ - $n\text{TiO}_2$  treatments, which are in good agreement with typical values reported in literature for pure anatase phase [11]. These results prove that no changes in the characteristic band gap energy values of nano- $\text{TiO}_2$  material occur upon interaction with silica gel network (i.e. formation of Si-O-Ti bonds, as evidenced by  $\mu\text{FTIR}$  data), and therefore the photocatalytic properties of  $n\text{TiO}_2$  are maintained. The only positive effect of the strong interaction is to favour the dispersion of the NPs onto the surface.



**Figure 4.** Magnification of micro-FTIR spectra of solvent-based TEOS (T75),  $\text{TEOS}$ - $n\text{TiO}_2$  treatment on wet surface (W-T75- $n\text{TiO}_2$ ) and on dry surface (D-T75- $n\text{TiO}_2$ ), showing the shift of the Si-OH absorption band from about 950 to 910  $\text{cm}^{-1}$ .

In conclusion, an easy way to develop a compatible self-cleaning  $\text{SiO}_2$ - $n\text{TiO}_2$  treatments is proposed, based on the use of a cost-effective consolidation material (TEOS). The methodology of application of  $\text{SiO}_2$ - $n\text{TiO}_2$  dispersion is a discriminating factor. The wet-on-wet  $\text{SiO}_2$ - $n\text{TiO}_2$  treatments exhibit different advantages. They show higher photocatalytic activity compared to the wet-on-dry ones and  $n\text{TiO}_2$ , due to the higher amount of NPs homogeneously distributed on the stone surface. The formation of a combined  $\text{SiO}_2$ - $n\text{TiO}_2$  layer, where the NPs are embedded in the  $\text{SiO}_2$  gel network, is supported by both ESEM-EDX observations of cross-sections and by the detection of Si-O-Ti interactions by  $\mu\text{FTIR}$ . Finally, promising results have been obtained so far by applying W-T100- $n\text{TiO}_2$  on marble tiles in a pilot-area of the façade of Monza Cathedral (Italy) and monitoring its effectiveness for 12 months [12]. Further researches are required to evaluate the supposed improvement of durability in outdoor real conditions.

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**Keywords:** stone conservation • self-cleaning • nano- $\text{TiO}_2$  • tetraethyl orthosilicate • photocatalytic

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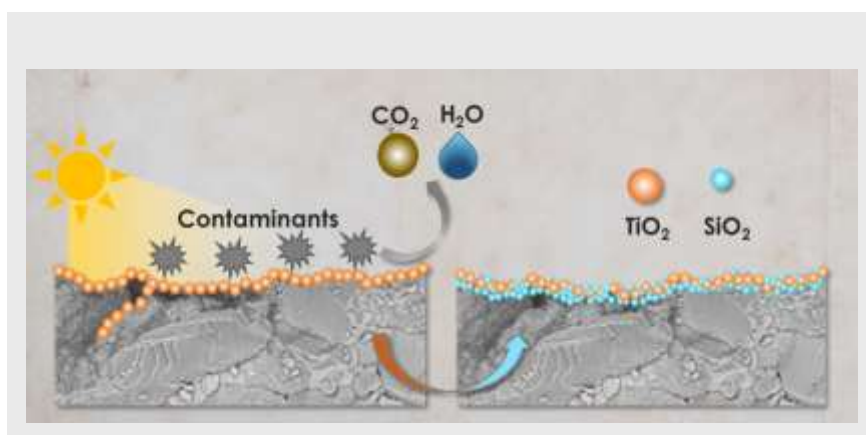
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Layout 2:

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Francesca Gherardi\*, Sara Goidanich  
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Layered nano-TiO<sub>2</sub> based treatments  
for the maintenance of natural stones  
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Layered treatments of natural stones based on dispersions of experimental nano-TiO<sub>2</sub> and commercial TEOS were set-up to avoid the penetration of NPs into the crystalline porous substrates and to improve their adhesion to the stone. The combined SiO<sub>2</sub>-nano-TiO<sub>2</sub> treatments demonstrate enhanced photocatalytic and self-cleaning properties compared to NPs dispersions.