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Innovative nano-TiO_2 particles for the preparation of self-cleaning treatments of historic architecture and sculptures

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SUMMARY: This research reports the results from the experimental testing of a new treatment based on water and ethylene glycol nano-TiO_2 dispersions with photocatalytic properties, that were tested on a calcarenite (Noto stone) and Carrara marble. To verify that the proposed treatments did not affect the intrinsic properties of the stones, colour measurements and water absorption by capillarity tests were carried out. The effectiveness of the photocatalytic activity of TiO_2 nanoparticles was evaluated by decomposition tests of organic colorants (Rodamine B), both after indoor exposition and after ageing in a Xeno lamp solar box. The results showed good efficiency and suitability for the use of nano-TiO_2 dispersions in the field of architectural heritage.

KEY-WORDS (maximum of five): nano-TiO_2 dispersions, self-cleaning, stone

INTRODUCTION

In order to provide crack-free materials and improve the consolidation and/or protection performance of different materials, nanoparticles are added to the consolidation products or employed as consolidants of stones and mural paintings. Different strategies have been implemented, by applying dispersions of nanoparticles of alkaline earth metal hydroxide or adding nanostructured SiO_2, Al_2O_3, TiO_2 in low and high molecular weight matrices [1,2].

In the last decades, a considerable part of the scientific research has been devoted to the synthesis of innovative coatings based on TiO_2 nanoparticles, which are employed to solve environmental problems regarding the purification of water and air from harmful compounds produced by industries, heating systems and traffic. The photocatalytic activity of TiO_2 prevents the accumulation of deposits given its properties to induce decomposition of polluting agents, either organic or inorganic, and the protection of the stone surfaces from deterioration processes. Moreover, it can establish a hydrophilic surface layer that increases the wettability of the surface on which they are applied. Because of these properties, these materials are defined as “self-cleaning” [3,4].

Commercial TiO_2-based coatings have several limitations and problems. Most of them require to be irradiated by an ultraviolet (UV) light source, in order to activate the TiO_2. However, there are few specific investigations of their application in the field of conservation of cultural heritage, as this requires long term durability tests, outdoor exposure of specimens in polluted areas and application on case-studies [5-6]. In order to improve these coatings, the synthesis of TiO_2 nanoparticles in benzyl alcohol is proposed so as to obtain pure anatase phase nanoparticles with an opportune surface capping, which makes TiO_2 photo-active not only under UV light but also under solar light [7].

EXPERIMENTAL PART

Materials and Methods

TiO_2 nanoparticles were synthesized according to the non-aqueous route, in which 4 mL of $TiCl_4$ (99.9%, Sigma Aldrich) are slowly added to 80 mL of anhydrous benzyl alcohol ($\geq$ 99.0%, Sigma Aldrich) under stirring at room temperature. Benzyl alcohol was previously degassed under vacuum at 120°C for 2 hours. Nanoparticles with the desired size were obtained using 80°C as reaction temperature and 24 hours as reaction time. The resulting white suspension was centrifuged and washed three times, twice with ethanol and once with tetrahydrofuran. Finally the nanoparticles were added to water and ethylene glycol, in order to obtain solutions with TiO_2 concentrations of 1%, 2% and 3 % by weight for water (WA) and of 1%, 2% and 4% w/w for ethylene glycol (EG), named WA1, WA2, WA3, EG1, EG2, EG4 respectively.

For comparison, water dispersions of commercial nano-TiO_2 (TiO_2 P25, Evonik AEROXIDE®) were also used. These nanoparticles are characterized by a crystalline composition with a ratio of 78:14:8 anatase–rutile–amorphous phase and the average sizes of the anatase and rutile elementary nanoparticles are 85 and 25 nm, respectively [8, 9]. These commercial titania were selected among different nano-TiO_2 available on the market because they are the most effective in terms of photocatalythic activity. TiO_2 nanoparticles were added to water and sonicated for 15 minutes in order to obtain concentrations of 1% , 2% and 3% by weight (called CA1, CA2 and CA3, respectively).

The nanosize TiO_2 dispersions were applied by brush on the surface of calcarenite (Noto stone) and Carrara marble samples with sizes 50x50x10 mm and 50x50x20 mm, respectively, previously washed with deionized water and dried. Not treated stone samples were also employed for comparison with treated ones (called REF).

The nanoparticle size and morphology 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 water TiO_2 dispersion onto a carbon coated copper 200 mesh grid. The morphology of the lithotypes before and after application of the treatments, as well as the penetration depth of the nano TiO_2 were analized by Scanning Electron Microscopy (ESEM) and EDX analyses using a Zeiss EVO 50 EP environmental scanning electron microscope, equipped with an Oxford INCA 200 - Pentafet LZ4 spectrometer.

The color change of the surfaces after the application of the treatments was assessed by VIS spectrophotometric measurements, carried out with a Konica Minolta CM-600D instrument, with a D65 illuminant at 8°, wavelength range between 360 nm and 740 nm. Measurements were elaborated according to the CIE L*a*b* standard color system, which describes a color with three different parameters, L*, a*, and b*, measuring respectively brightness, red/green and yellow/blue color intensities. Ten measurements were performed on each area and the average results of L*a*b* were used to calculate the color difference ΔE* between treated and untreated areas ($\Delta E^* = [(L^*_2-L^*_1)^2 + (a^*_2-a^*_1)^2 + (b^*_2-b^*_1)^2]^{1/2}$).

The photocatalytic activity of TiO_2 nanoparticles was verified by means of the decomposition of an organic colorant (Rhodamine B, rB) test, both after indoor exposition of the treated samples and after ageing in a solar box with a Xeno lamp. The rhodamine B water solution (0.05 g/l ± 0.005 g/l) was applied on the surface of both untreated and treated samples (1 ml per specimen), then, after drying, colorimetric measurements were carried out using a VIS spectrophotometer (Konica Minolta CM-600D instrument, as described above). The degradation of the applied organic dye was monitored by evaluating the color change of the surfaces exposed indoors 70 cm from a window exposed east in Milan from September to March after 1, 17, 26, 120, 312, 528, 696, 1968 and 4128 h. The degradation of rhodamine B was also evaluated on samples aged in a solar box, Suntest CPS+ equipped with a Xenon arc lamp source and a cut off filter for wavelengths below 290 nm. The irradiation was kept constant at 765 W/m^2, at a distance of 20 cm and temperature was maintained at 35°C. The aim of the test was the photoactivity evaluation of TiO_2 after solar irradiation. Indeed, in order to better simulate the real condition of treated and outside exposed stones, it was decided to use a Xeno lamp, instead of an UV lamp, because it has a spectral emission similar to that of solar light. The color changes of the surfaces were monitored after 15, 30, 60, 90 and 150 minutes of irradiation. Only the chromatic coordinate a^* was used to evaluate the photocatalytic discoloration of stain over time ($D^* = (|a^*(t) - a^*(rB)|/|a^*(rB) - a^*(0)|*100$, where $a^*(0)$ and $a^*(rB)$ are the average values of chromatic coordinate a* before and after the application of the stained solution and $a^*(t)$ is the a* value after t hours of light exposure).

Static contact angle and capillary water absorption tests were carried out in order to evaluate the changes of the wettability and water absorption of the stone surfaces after the application of the nano-TiO_2 dispersions. Static contact angle test was performed on 15 points for each sample, according to UNI standard [10], using an OCA (Optical Contact Angle) 20 PLUS (DataPhysics, Germany), with a drop volume of 5 µl, after 10 seconds. Drop shape was recorded with a camera and the angle between the substrate surface and the tangent from the edge to the contour of the water drop (contact angle) was evaluated. The capillary water absorption of the stone samples before and after the application of the treatments was performed according to UNI standard [11] on 50x50x20 mm samples of Noto stone and Carrara marble. This test consists in the determination of the capillary water absorption of the sample in contact with deionized water. The capillary water absorption value per unit area (Q_i, expressed in mg/cm^2) is defined with this formula: $Q_i = (m_i - m_0)/A*1000$, where m_i is the mass (g) of the wet sample at time t_i, m_0 is the mass (g) of the dried sample, A is the surface area (cm^2) in contact with the water. The samples were weighed at the following time interval: 10 min, 20 min, 30 min, 60 min, 4 h, 6 h, 24, h, 48 h.

RESULTS AND DISCUSSION

Characterization of TiO_2 dispersions

To study size and morphology of the synthetized TiO_2 nanoparticles, the water TiO_2 dispersions at 3% w/w concentration were analysed with TEM. As shown in Figure 1, it is possible to identify the presence of primary nanoparticles of anatase of about 5–6 nm, aggregated in elongated structures whose the longest axis measures about 40 nm. Moreover, these structures do not further aggregate but have an homogenous distribution.

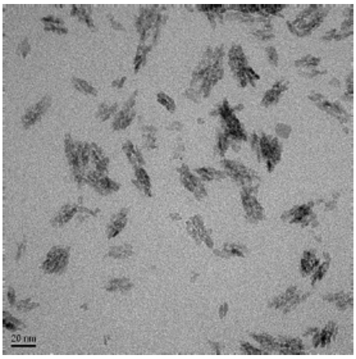

Figure 1. TEM image of 3 % w/w water TiO_2 nanoparticles.

Evaluation of the effectiveness of the treatments

In order to evaluate the maintenance of the aesthetic properties of the stones after the application of the synthetized TiO_2 dispersions, colorimetric tests were performed. The results, in terms of ΔE* values for each treatments (WA1, WA2, WA3, EGA1, EGA2, EGA4, CA1, CA2, CA3) and for each substrate are reported in Table 1.

As shown, ΔE* values for the Noto stone samples treated with the commercial water dispersions of nano TiO_2 at 2% and 3% w/w (CA2, CA3) are far higher than 5, the acceptable limit of ΔE* value for restoration treatments in the field of cultural heritage. Therefore they are not suitable for restoration purpose and for this reason, only the CA1 treatment with commercial nano TiO_2 at 1% w/w was used to be compared with the other tests. For Noto stone, after the application of the new treatments, ΔE* values are lower than 0.69±0.56, while for Carrara marble the ΔE* values are lower than 1.35±0.91. The obtained results show that the nano TiO_2 treatments do not modify the original color of the stone surfaces, since color variations with ΔE* values lower than 1 are not visible to naked eye.

The photocatalytic properties of the new TiO_2 dispersions were evaluated with tests of decomposition of rhodamine B, both after indoor exposition of the treated samples and after ageing in solar box with a Xeno lamp.

Table 1. ΔE* values of Noto stone and Carrara marble specimens before and after the application of TiO_2 treatments.

	ΔE	
	Noto stone	**Carrara marble**
WA1	0.12±0.08	1.02±0.51
WA2	0.40±0.12	1.35±0.91
WA3	0.16±0.01	1.19±0.64
EGA1	0.22±0.02	1.23±0.28
EGA2	0.33±0.12	1.12±0.18
EGA4	0.69±0.56	0.83±0.39
CA1	3.60±1.40	1.27±0.65
CA2	8.73±3.49	/
CA3	8.91±3.61	/

The fading of the organic colorant was monitored by color measurements over time and the values of the stain discoloration D* (D* = (|a*(t) – a*(rB)|/|a*(rB) – a*(0)|*100) as a function of exposure time (h) are shown in Figure 2. The D* values show a greater slope in the first hour of exposure, then the values reach a plateau because the degradation kinetics of the red dye slows down. It should be noted that the D* values of the reference sample also increases with time, probably because of the effect of the light on the degradation of rhodamine B, however D* values of the treated sample are always higher than the ones of the reference because TiO_2 treatments promotes and accelerates the degradation of the colorant. For instance, in the first hours of exposure, the D* values of the samples treated with EGA4 are 60% higher than the D* values of the reference while at the end of the test the difference between the two values are about 30%. For the case of the treated samples, at equal exposure times, those treated with ethylene glycol TiO_2 dispersions at higher concentrations (EGA2 and EGA4) are more photocatalytic than the samples treated with water dispersions, even if at the end of the test the differences between the results of the different treated samples become smaller.

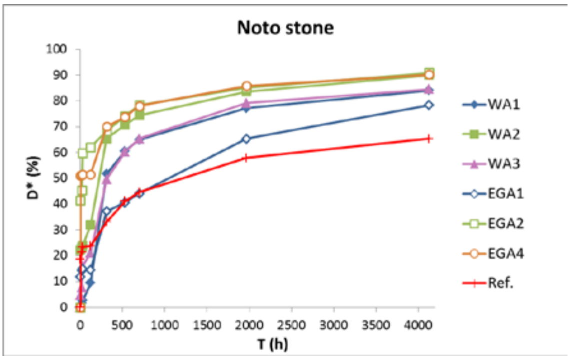

Figure 2. Stain discoloration values D* (%) as a function of time (h) for Noto stone samples after indoor exposition to solar light.

Another equivalent set of treated Noto stone and one of treated Carrara marble specimens was aged in a solar box with a Xeno lamp, in order to evaluate the photocatalytic activity of the samples in short time. The obtained results are shown in Figure 3 and, similarly to the previous test results, the stain discoloration D* values increase faster during the first minutes of light exposition. For Noto stone, the best results in terms of photocatalytic activity were achieved for samples treated with the highest TiO_2 concentration dispersions (WA3 and EGA4), whereas for Carrara marble the highest fading of the colorant was achieved by samples coated with ethylene glycol nano-TiO_2 dispersions, particularly EGA4. Comparing the stain discoloration curves for the Noto stone and Carrara marble, it is clear that the degradation of the colorant on marble samples is much faster. In fact, during the first 15 minutes, the stain discoloration D* of marble samples treated with EGA4 reaches almost 70% while in Noto stone samples treated with EGA4, D* reaches 38%. This could be explained by the fact that a lower concentration of nano TiO_2 is present on the surface of the Noto stone specimens because of the deep penetration of the nanoparticles into the substrate. The D* values of the treated samples are higher than the ones for the references. This indicates that the nano-TiO_2 dispersions are able to accelerate and promote the degradation of the soiling, in agreement with the results obtained by indoor exposure of the samples to solar light (Figure 2). As shown in Figure 3, the new water and ethylene glycol treatments are more effective than commercial titania in terms of photocatalytic activity. Indeed, even if in the first minutes the commercial nanoparticles are more photocatalytic than the reference, at the end of the test they reach quite the same value of stain discoloration D*, especially in Carrara marble samples.

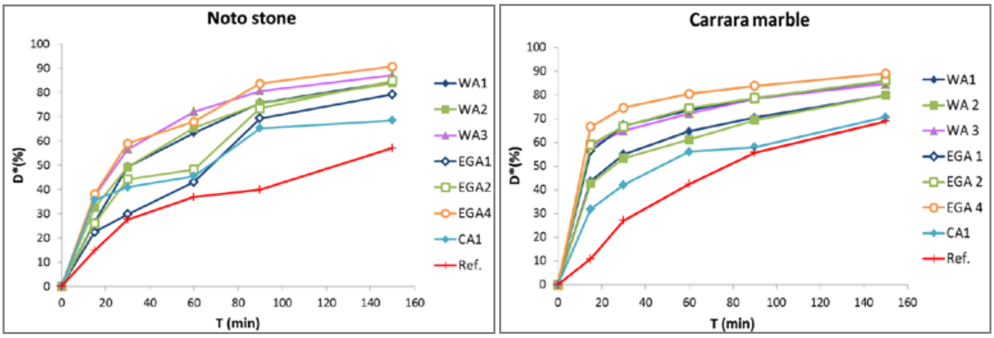

Figure 3. Stain discoloration values D* (%) as a function of time (h) for Noto stone (left) and Carrara marble (right) samples after ageing in solar box with a Xeno lamp.

In order to verify that the application of nano-TiO_2 treatments did not affect the wettability, static contact angle measurements were carried out. It is important to remember that these treatments were not designed to change the wettability of the surfaces and therefore no differences are expected in this property when compared to the reference samples. In the case of the Noto stone, because of its high porosity, it was not possible to carry out the measurements because the water drop was lost within the first 10 seconds. The values of static contact angles of treated and untreated Carrara marble samples are presented in the diagram in Figure 4. Apart from the untreated reference sample a second reference (REF_EG) was prepared by treating it with ethylene glycol to compare its contact angle value with that of samples treated with nano TiO_2 dispersions in ethylene glycol. The contact angle values of the samples treated with water and ethylene glycol dispersions are lower than the ones of the reference sample (REF and REF_EG respectively). This means that the new synthetized titania slightly alters the wettability, making the stone surfaces more hydrophilic than the references, thus improving their self-cleaning skills. However, samples treated with the water dispersion of commercial nano TiO_2 show a higher static contact angle value than the untreated reference sample (REF) and similar to that of the reference sample treated with ethylene glycol. They do not achieve the same surface hydrophilicity as the new synthesized titania water treatments. This should be related to the fact that without UV irradiation, the commercial titanium dioxide does not show photo-induced hydrophilic properties, while the new synthetized nano TiO_2 is photo-active also under regular solar light exposure. The standard deviations of these values are also higher than the other results, indicating that the surface is very irregular and inhomogeneous. This could be attributed to the aggregation of commercial nanoparticles that leads to an irregular distribution of titania and to an increase of the roughness of the stone surface.

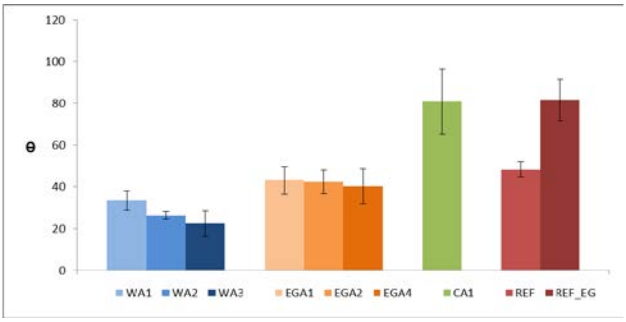

Figure 4. Contact angle values of Carrara marble samples, treated with new synthetized titania treatment (WA1, WA2, WA3, EGA1, EGA2, EGA4), with commercial titania (CA1, CA2, CA3), untreated reference (REF) and reference treated with ethylene glycol (REF_EG).

Capillary water absorption curves for Noto stone and Carrara marble samples, before and after the application of new synthetized and commercial nano-TiO_2 treatments are shown in Figure 5. The results show that there is no significant difference between the curves measured before and after the application of nano TiO_2 dispersions. The Q_i values differ between the samples because of physical properties such as porosity and roughness rather than because of the nano TiO_2 treatments. This confirms that the presence of nano TiO_2 does not alter the water absorption by capillarity of the samples. The only exception is represented by Carrara marble samples treated with ethylene glycol TiO_2 dispersions (Figure 5 d), that seem to show a slight reduction in the water absorption.

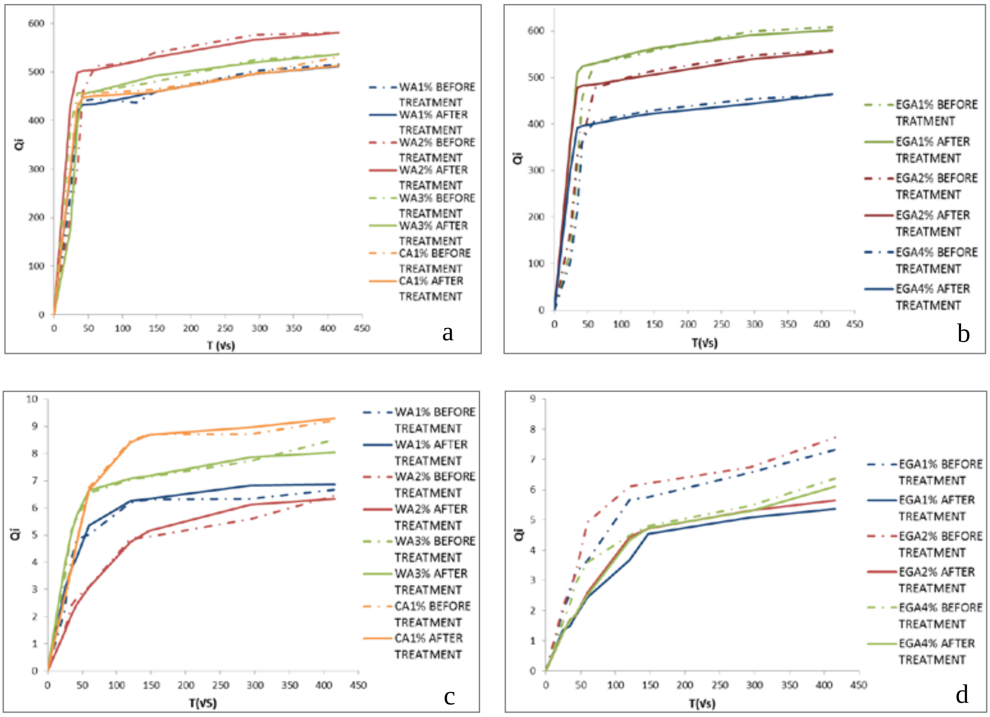

Figure 5. Water absorption by capillarity before (dashed lines) and after (solid lines) the application of the titania water and ethylene glycol dispersions on Noto stone (a and b) and on Carrara marble (c and d).

Evaluation of the penetration depth of titania treatments

The surface and the section of small specimens of untreated and treated Noto stone and Carrara marble samples were analyzed by SEM-EDS, in order to study the morphology and the penetration depth of the titania treatments. The distribution of new water and ethylene glycol nano-TiO_2 dispersions on Noto stone surfaces was not homogeneous, because the physical features of the stone (porosity, roughness) lead to the aggregation of the titania mostly inside pores, even in depth. On the contrary, on Carrara marble specimens, the TiO_2 treatments create a continuous film on the surface with no cracks,. Moreover by observing the sections, on Carrara marble specimens the new treatments were present only within the first microns, whereas their penetration depth in Noto stone samples was about 300-500 µm. The porosity of the Noto stone results in the penetration of the nanoparticles into the sample thus reducing the amount of photocatalytic titania on the surface. A possible way to prevent the penetration of TiO_2 nanoparticles into porous substrates could be to apply the titania dispersions after a pre-treatment with a consolidant. To evaluate this solution, some tests are currently under way.

CONCLUSIONS

The study focused on new photocatalytic treatments based on water and ethylene glycol nano-TiO_2 dispersions at different concentrations, applied on Noto stone and Carrara marble. Water dispersions of commercial titania nanoparticles were also evaluated for comparison with the new proposed treatments. Colour measurements assessed that the new treatments did not alter the aesthetic properties of the stones, unlike the commercial ones.

Static contact angle and capillary water absorption tests showed that there were no significant differences after the application of the new treatments. The static contact angle values of the samples treated with synthetized titania dispersions were lower than the values of untreated samples and of samples treated with commercial dispersions, indicating that the new treatments improve the self-cleaning properties of the stone surfaces.

Regarding the photocatalytic activity, the results show that the synthetized titania nanoparticles are photo-active not only under UV light but also under solar light and they are therefore more effective than commercial titania. These photocatalytic materials are suitable for building restoration purposes because they promote the degradation of both polluting agents and soiling, limiting the frequency of conservation interventions on materials, thus decreasing maintenance costs.

Further laboratory and monitoring tests (color measurements) on treated samples exposed outside to weathering are currently underway, in order to evaluate their durability and capacity as self-cleaning treatments for the conservation of cultural heritage.

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