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Article

Preservation of Historical Stone Surfaces by TiO_2 Nanocoatings

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Abstract: We proposed the application of titanium dioxide (TiO_2) for the preservation of historical (architectural, monumental, archaeological) stone surfaces. Solar light can activate the photocatalytic effect of TiO_2 nanoparticles: heterogeneous photocatalysis is the key factor for the development of self-cleaning, depolluting and biocidal treatments able to photochemically degrade external damaging materials and prolong the durability of treated substrates, maintaining their original aspect and limiting ordinary cleaning activities. In this study, TiO_2 nanoparticles dispersed in an aqueous colloidal suspension were applied directly on travertine, a light-colored limestone, by spray-coating in order to obtain a nanometric film on stone samples. To assess the feasibility of use of TiO_2, we studied the characteristics of the nanocoating-stone system by monitoring the microscopic features of the coatings, the aesthetical changes induced to coated surfaces and the self-cleaning efficiency. We also monitored the self-cleaning ability over time during an accelerated ageing process to evaluate the durability of TiO_2-based treatments. We confirmed both compatibility and effectiveness of TiO_2 coating in the short term, anyway its efficiency decreased after artificial ageing. Further studies are necessary to better evaluate and eventually improve the stability of self-cleaning efficiency over prolonged time for outdoor stone surfaces.

Keywords: titanium dioxide; photocatalysis; architectural and archaeological heritage; self-cleaning coating; durability

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1. Introduction

The use of nanotechnological solution to better preserve historical and artistic items as well as architectural, monumental and archaeological elements is greatly increasing nowadays. Titanium dioxide is among the most important and widespread nanoproduct used in the building sector [1,2] mainly because of its photocatalytic effect [3–7]. Photocatalysis—the activation of redox reactions by light—may cause the degradation of several pollutants and the killing of biotic factor of decay, thus allowing an easier removal of soiling, biological stains and biofouling from surfaces, including architectural ones [8–13]. The presence of soiling may cause not only visual nuisance, since stains and biological material are potentially harmful for several materials, including stones [14–16]: that is especially true for architectural and archaeological surfaces vulnerable to weathering.

Titanium dioxide (TiO_2) nanoparticles activated by solar light may be potentially applied even on pre-existing surfaces—a requisite for their potential use in the field of restoration—to longer maintain the original characteristics of treated substrates [13,17–21]. Brushing and spray-coating are by far the most used methods to apply the solutions containing nanometric TiO_2.

In this study, TiO_2 nanoparticles dispersed in an aqueous colloidal suspension have been applied directly on travertine, a porous limestone, by spray-coating in order to obtain a nanometric film over the stone surface. To assess the feasibility of use of TiO_2 on stone architectural surfaces, we studied the characteristics of the nanocoating/substrate system by monitoring the microscopic features of the coating, the aesthetical changes caused to coated surfaces and the photoactivity of TiO_2 thin film. Photocatalytic activity of the coating was assessed by self-cleaning test. We also monitored the self-cleaning ability over time during an accelerated ageing process to evaluate the photoactivity and the durability of TiO_2-based treatments in the long term. The work we present here is the synthesis of our investigations on this topic.

2. Experimental Section

2.1. Application of TiO_2 Nanoparticles

TiO_2 aqueous colloidal suspension (sol) having a TiO_2 content of 1 wt% was obtained by sol-gel method. Tetrapropyl orthotitanate (TPOT, Sigma Aldrich 97%, St. Louis, MO, USA) was used as TiO_2 precursor; it was added dropwise to biidrate oxalic acid (Carlo Erba Reagents 99.8%, Cornaredo, Italy) dissolved in deionized water. The resulting precipitate was dissolved by warm stirring thus forming a TiO_2 amorphous sol. The amorphous sol was processed in autoclave (temperature: 125 °C, pressure: 3.5 bar) to obtain TiO_2 nanocrystals in the anatase phase. The average crystalline size of the product was about 4 nm as estimated by XRD analysis; anyway dynamic light scattering (DLS) and transmission electron microscopy (TEM) performed in previous analyses of the same sol noted a final aggregation of original nanoparticles up to a size of about 40–50 nm.

The sol was applied through spray-coating on travertine, a porous limestone largely used for monumental and historical buildings as well as artistic elements and still used in the construction sector. Spray-coating was selected because of its simplicity and compatibility with pre-existing surfaces.

Previous studies demonstrated the non-linear correlation between performances and TiO_2 content in the sol or TiO_2 amount deposited on the substrate [21]. On the other hand, we decided to cover the stone with subsequent layers of nanoproduct to better simulate its application in real-cases, when the difficulty of spreading the nanoparticles uniformly on substrates because of outdoor conditions suggests applying the sol by means of consecutive spraying cycles.

Three layers of sol were consecutively applied by a spray gun (air pressure: 6–8 bar, nozzle diameter: 1.5 mm, sol content per layer: 1.8 mL) on stone samples (dimensions: 8.0 × 8.0 × 1.5 cm^3) previously dried until constant mass—*i.e.*, until the difference between two consecutive weight measurements was inferior to 0.1%—and the amount of deposited sol was determined by weight. The average amount of TiO_2 deposited on stone samples was about 0.60 g/m^2. Untreated samples were used as references. Three samples were used for each series (treated and untreated).

2.2. Microanalysis of the Coating

The microstructure of the coating/substrate system was investigated by scanning electron microscopy (SEM, Quanta-200 instrument, FEI, Hillsbro, OR, USA) and energy dispersive X-ray spectroscopy (EDX, INCA 350, Oxford Instruments, Abingdon, UK) to establish both the morphology of the coating (secondary electron analysis, SED) and the presence of TiO_2 particles (backscattered electron analysis, BSD). A thin gold layer was deposited before microscopic analysis. Further, specific details about single microscopic investigations are reported in Section 3.1.

2.3. Compatibility between TiO_2 Nanocoating and Travertine

Because of their potential use for the preservation of architectural heritage, the presence of nanocoatings should not alter the visual aspect of treated substrates too evidently. The color difference caused by the application of TiO_2 was monitored and defined as ΔE^* according to CIE (Commission internationale de l'éclairage) $L^*a^*b^*$ (CIELAB) system:

$$\sqrt{(L_{\mathrm{BT}}^* - L_{\mathrm{AT}}^*)^2 + (a_{\mathrm{BT}}^* - a_{\mathrm{AT}}^*)^2 + (b_{\mathrm{BT}}^* - b_{\mathrm{AT}}^*)^2} \qquad (1)$$

wherein L^*, a^* and b^* are the parameters defining the color intensity (respectively in the black-white, green-magenta and blue-yellow axis of the CIELAB color space) before (BT) and after (AT) treatment.

A portable spectrophotometer (Konica Minolta CM 2600 d, Tokyo, Japan) was used to measure the color of both treated and untreated surfaces [22]: nine points defined by a planar grid were randomly selected for each specimen; color difference due to TiO_2 for each coated sample was defined as the difference between the average color of the sample before and after the spray-coating. The threshold value considered acceptable for compatibility with historical or monumental surfaces is conventionally set to $\Delta E^* = 5$ [20,23,24].

2.4. Preservative Effect of TiO_2 Nanocoating: Efficacy and Durability over Time

The photocatalytic effectiveness of TiO_2 nanoparticles applied to better preserve the aspect of stone substrates over time was assessed by means of a self-cleaning test [25]. Rhodamine B was dissolved in water (0.05 ± 0.005 g/L) thus obtaining an artificial dye, then the solution was applied on stone surfaces in order to simulate soiling. Stained samples were put into a dark container for 24 h to let the dye dry and then they were exposed to UV light (blacklight lamp; wavelength range: 350–400 nm; irradiance value on stone surfaces: 4 W/m^2) for another day. A scheme of the equipment used during the test is reported in Figure 1. To better simulate the real use of photocatalysis under natural daylight the value of UV irradiance used during test—as defined by standard rule—is equivalent to a quite weak natural UV illumination, far less than high-intensity possible irradiation on Earth's surface [26].

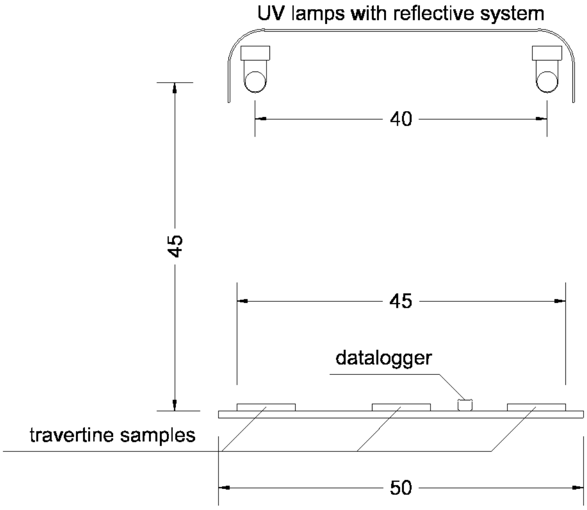

Figure 1. Diagram of the laboratory system used to perform the self-cleaning test.

We checked the color of the stains over the 24 h-long test under UV illumination to assess the self-cleaning effect of TiO_2 before the exposure to UV light and after 1, 4 and 24 h of illumination (three measurement points for each sample). To define the intensity of self-cleaning ability R^*_E, the color of stains was referred to the original aspect of stone [27]:

$$R^*_E = \frac{|\Delta E^*_t - \Delta E^*_0|}{\Delta E^*_0} \times 100 \tag{2}$$

where ΔE^*_t and ΔE^*_0 were respectively the color changes—as defined in (1)—at given time t during test (after 1, 4 and 24 h of UV irradiation) and at the beginning of self-cleaning test (t = 0 h) after the application of rhodamine B with reference to the original color of travertine (after coating deposition in case of treated surfaces).

Temperature and relative humidity under UV illumination were monitored over time; they ranged from 18.9 to 20.5 °C and from 54.2% to 57.2% respectively.

Furthermore, to better evaluate the extended use of self-cleaning coatings in outdoor conditions, we artificially simulate the ageing caused by natural ultraviolet irradiation over time. The durability of photoactivity can be very important for architectural and archaeological treated surfaces exposed to natural weathering over time. The ageing effect in the outdoor environment is usually related to separate weathering agents and their potential synergic outcome. Durability of nanocoatings has been poorly investigated until now: in order to simplify the accelerated ageing process and to obtain clear results at the end of the preliminary analysis independent on multiple criteria and parameters, only the ageing related to prolonged solar exposure typical of outdoor conditions (an usual agent causing stress to coating materials) was studied. Because of the semiconductor nature of TiO_2 and its ability to strongly interact with other substances by redox mechanisms under UV light, the photochemical stability of TiO_2-containing materials over time is a crucial feature to investigate. In our analysis, this characteristic was indirectly monitored by the evaluation of its photoactivity via the self-cleaning test. Furthermore, since stone is usually not greatly altered by simple solar irradiation, the evaluation of the characteristics of TiO_2 nanoparticles over time is scarcely influenced by possible modifications of treated substrate.

Solar ageing was simulated through prolonged exposure to UV light, since UV rays are the most damaging part of solar irradiation. Very intense UV illumination (blacklight lamp; wavelength range: 350–400 nm; irradiance value on stone surfaces: 60 W/m^2) was used in order to simulate the possible decay resulting from the exposure to solar light. At the end of accelerated ageing (a total of about 1000 h) both treated and untreated surfaces were exposed to an eventual amount of UV rays comparable to about 9 months of solar exposure in Florida [28]. Self-cleaning test was then repeated to evaluate the possible loss of photoactivity due to artificial ageing.

3. Results and Discussion

3.1. Microanalysis of the Coating

The presence of TiO_2 nanoparticles over stone surface were clearly confirmed by SEM/EDX analysis (Figure 2). From the section analysis the thickness of the coating formed by the aggregation of ultrafine TiO_2 can be regarded as falling roughly into the 5–10 μm range (an example of measurement deduced from BSD image is given in Figure 2). The coating was homogeneously spread over stone but its surface was evidently cracked (Figure 2): this outcome may be related to the amount of TiO_2 deposited and the subsequent thickness of the coating, over the critical thickness of crack development [29]. It is important to notice by the comparison of the SEM images reported in Figure 2 that cracks were not uniformly present all over the coating but they were present in a punctual manner.

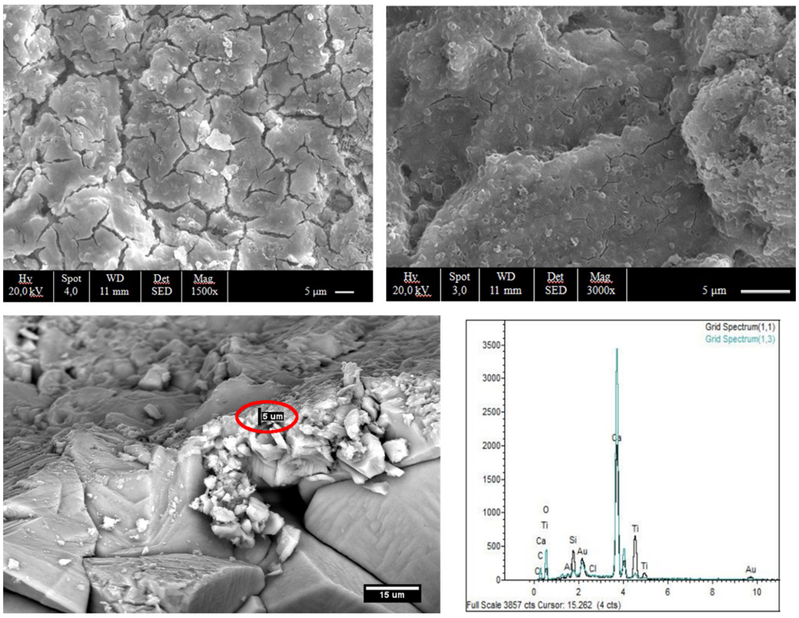

Figure 2. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) analysis of treated samples: surface morphology (SED, magnitude 1500× and 3000×); cross-section (BSD, titanium is colored bright white) with a reference scale for measuring the thickness of the coating and EDX spectra (two different measurement points). Details about the parameters (voltage, spot size, working distance) set during the analysis are also reported.

The EDX investigation carried out in various measurement points confirmed the presence of titanium over the entire analyzed surface, although in different quantities. In some cases titanium was the second element detected after calcium (one of the element of which travertine is made up). Untreated samples did not exhibit titanium in their EDX spectra (this result is not shown), so its presence on treated surfaces can be related only to the coating irrespective of the nature of stone substrate.

3.2. Compatibility between TiO_2 Nanocoating and Travertine

The average color change caused by TiO_2 deposition was $\Delta E^* = 2.36$. This value is fully compatible with their use for Architectural Heritage and, more specifically, with the requirements of the maintenance field. The chromatic variation can be considered noticeable by human eye [30] but it is clearly lower than the threshold limit ($\Delta E^* = 5$) required for the maintenance and restoration of historical or monumental surfaces.

Brightness (L^* coordinate in the CIELAB system) is the aesthetical parameter most influenced by the coating (Figure 3): nanometric TiO_2 particles alter the aspect of substrate in a way strongly restrained in comparison with greater TiO_2 particles normally used as a white pigment, anyway the brightening effect of TiO_2 is still the most evident even in the nanocrystalline form. The main reason behind the transparency of TiO_2 nanocoatings is the reduced size of ultrafine TiO_2: unlike the highly reflective conventional pigmentary TiO_2, TiO_2 nanoparticles scarcely interact (e.g., by means of scattering or absorption) with visible light since their size is smaller than visible wavelength that is virtually transmitted through the nanomaterial [31].

The proved transparency of studied nanocoating is compatible with stone substrate and allows its use as a protective system for historical or artistic surfaces of Architectural Heritage without excessively (or negatively) altering their aspect to the naked eye.

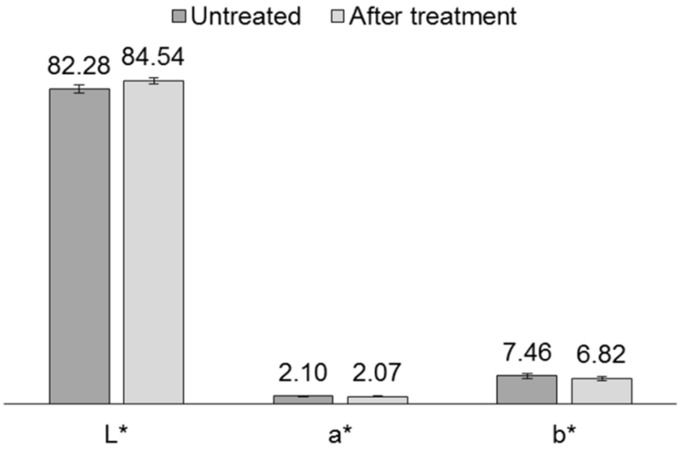

Figure 3. Average chromatic values according to CIELAB system before and after TiO_2 treatment.

3.3. Self-Cleaning Ability of TiO_2 over Time

The photoactivity of multi-layer coating was clearly evident before ageing (Figure 4). During the exposure to weak UV light the most part of stains was visually removed by the self-cleaning effect of the coating. The main part of the photodecoloration occurred in the first hours of exposure to UV illumination as shown by the values $R_E^*(1)$ and $R_E^*(4)$, then the photocatalytic reactions became slower. Untreated surfaces did not show significant changes in their aspect over time (Figure 4), so the removal of stains by treated surfaces can be considered the effective photodecoloration by TiO_2 nanoparticles and not a deteriorating effect solely related to ultraviolet light. This finding strongly suggests that in the short-term, TiO_2 nanocoatings may be very effective as a preventive treatment to preserve the aspect of stone surfaces.

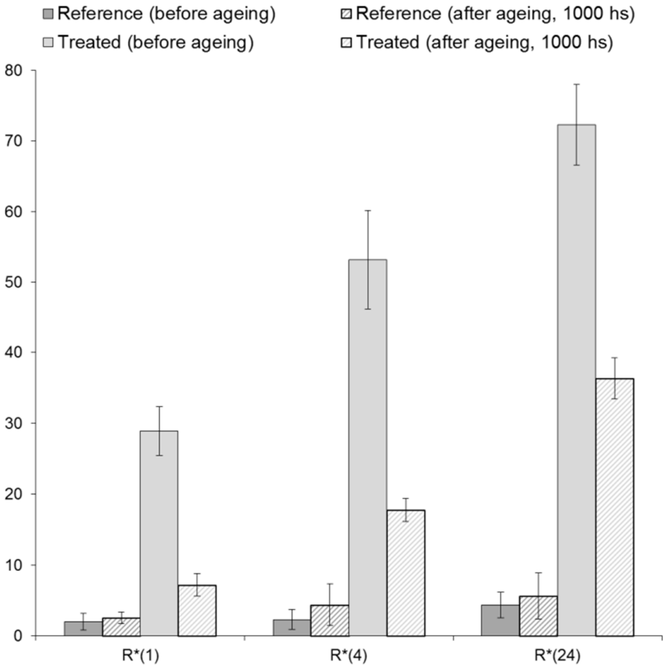

Figure 4. Average values of the parameter R_E^* describing the intensity of self-cleaning efficiency during test procedure (after 1, 4 and 24 h of exposure to UV light) on treated and untreated surfaces. The results refer to the performances measured at time zero (before ageing) and at the end of the 1000 h-long weathering procedure (after ageing).

It is important to notice that the presence of the microscopic cracks seems to not influence or limit the photoactivity of the coating and its use as a self-cleaning preserving product.

After the ageing process, the self-cleaning effect of the coating was clearly reduced. Initial test conditions—*i.e.*, the color of stains at the beginning of self-cleaning test—were very similar but at the end of self-cleaning tests the decoloration by aged coating was evidently inferior in comparison with pre-ageing results. The artificial weathering affected mainly the first part of the photodecoloration process making it clearly slower, while the kinetic of the remaining part of the test (after 4 h of UV light exposure) was nearly unaltered. This reduction in the photoactivity of TiO_2 was confirmed by the homogeneous behavior of treated samples after ageing, as shown by their lower standard deviation values in comparison with time-zero results (Figure 4).

The behavior of uncoated surfaces was barely affected by ageing and the decoloration of rhodamine B under weak UV irradiation remained negligible. Travertine itself did not alter its behavior towards rhodamine B under UV so it seems reasonable to suppose that stone substrate did not directly influence coating durability. The reduced efficiency of the coating over time noted on treated surfaces should be related to coating modifications or interactions independently of characteristics of mere travertine.

Probably TiO_2 deactivation is mainly caused by deposition of surface species, intermediates, hydroxyl radicals, chemical by-products (including the remains of the pre-ageing self-cleaning test) which are difficult to decompose [2] and may strongly interact with photoexcited TiO_2 under UV light. Furthermore, the decrease of TiO_2 photoactivity could be related to some changes in the oxygen vacancy numbers [32].

In conclusion, even in the long-term stones coated with TiO_2 nanoparticles exhibit a better behavior in comparison with reference surfaces and a partially preservative effect against soiling towards treated substrate. Anyway, the reduced effectiveness of self-cleaning ability limits the potential use of pure TiO_2 coatings to preserve architectonic and archaeological surfaces exposed in outdoor conditions. Supplementary weathering simulations and the use of better performing additives are necessary to solve the durability issue.

4. Conclusions

In this work, we studied the use of titanium dioxide as a protective coating for stone surfaces of architectural and archaeological interest to impede the formation of potentially harmful soiling.

The application of TiO_2 nanoparticles does not alter the aspect of stone in a relevant way: this is a basic characteristic to estimate the compatibility with substrates having artistic value.

Furthermore, in the short term, the photocatalysis of TiO_2 applied on stone is very efficient and able to degrade the most part of the soiling applied on treated surfaces. On the other hand, the nanoparticles seem to lose a relevant part of their photoactivity in the long term after an accelerated weathering process. Further investigations are necessary to better establish the durability of the self-cleaning effect and the lifespan of TiO_2 nanocoatings to suggest the eventual formulation of more durable sols.

Author Contributions

G.B. Goffredo and P. Munafò conceived and designed the experiments; G.B. Goffredo performed the experiments; G.B. Goffredo and P. Munafò analyzed the data, Salentec srl contributed reagents and materials; G.B. Goffredo wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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