



Durability assessment of nanostructured TiO₂ coatings applied on limestones to enhance building surface with self-cleaning ability



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ABSTRACT

Coating with nanostructured Titanium dioxide is able to enhance natural stone surface with self-cleaning and depolluting abilities; nonetheless, the durability of the coatings is a crucial issue to be assessed in relation to their potential for use in the context of the building heritage. In this paper, the resistance of coatings applied on a compact and a soft limestone, which differ in roughness, porosity and cohesion features, has been investigated. A peeling and a water impact test were performed and their effect on the coated surface was evaluated as film loss by qualitative/quantitative ESEM-EDS analyses. Self-cleaning effectiveness was assessed by performing a photodegradation test of Rhodamine B. Crack-free and conformable films showed a good anchorage to both limestones; after the durability tests the coated surfaces exhibited almost unchanged Ti/Ca ratios and self-cleaning efficiencies. Large adhesion failures and decreased Ti amounts were recorded where coatings were fissured; they especially occurred on the surface of the compact limestone, along with a reduced self-cleaning ability. High surface roughness accounted for a better adhesion of both crack-free and fissured films to the soft limestone, but some erosion of the coated surface, which affected this friable stone under the water impact, compromised their preservation. Nonetheless, good self-cleaning performances were still provided due to the retention of nanoparticles under the surface.

The overall results support that preservation of nanostructured TiO₂ coatings on the stone surface depends on the inherent characteristics of both films and supports; durability of the stone itself can play an important role.

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1. Introduction

Growing environmental pollution and its impact in many fields involve the modern society in the research and development of new technologies and processes for environmental protection and remediation. In this regard, innovative systems and solutions have been successfully proposed, based on the application of the heterogeneous Titanium dioxide photocatalysis [1–6]. It is an environmental friendly process consisting of a complex of reducing and oxidative reactions, promoted by hole - electron pairs created in the TiO₂ semiconductor under UV excitation by means of the absorption of light energy. These photo-induced reactions are able to degrade a wide range of either organic [7–9] and inorganic [10–12] contaminants, as well as microorganisms [13,14], in both water and

gas phases. Also photo-induced super-hydrophilicity is related to the TiO₂ photocatalytic activity [3,15].

In building industry, implementation of the TiO₂ photocatalysis has promoted a variety of novel materials, having surfaces functionalised with depolluting [5,16,17], self-cleaning [18] and anti-microbial properties [19,20]. Photocatalytic glass [21,22], ceramics [23,24] cements and mortars [25,26] have been obtained using titania nanoparticles (NPs) either applied as surface coating or embedded in bulk.

Application of TiO₂ as coating of natural stone has been successfully proposed in recent years [27–30]. Good self-cleaning and depollution efficiencies obtained on the coated surfaces indicate that functionalisation of building stones with photocatalytic properties can be effective to preserve building façades in polluted urban sites against the deposition of airborne matters, which compromises both the aesthetical appearance and durability of the stone surface. Such an approach could support a new strategy for preserving an extended stone building heritage and limiting the

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expensive charge for its maintenance. In addition, due to the wide use of natural stones within a large historical-architectural heritage of many countries, buildings are potential vehicles for a very wide surface exposition of photoactive TiO_2 in urban sites contributing to air cleaning.

In this regard, many studies have been implemented in the field of the photocatalytic oxidation technology of building materials for air purification [31] and they support air cleaning performance in relation to various gaseous contaminants including NO , NO_2 , SO_2 , CO [32,33], toluene, and so on [17,34]. In realistic environmental conditions, NO_x concentrations [35,36] and car exhaust gases [32] decrease with the use of photocatalytic materials in tunnels or streets and roads.

Nonetheless, there are still some fundamental issues related to the technology of photocatalytic building materials that need further research, e.g. durability of the coatings, which is a crucial aspect in evaluating their real potential for use in outdoor conditions.

TiO_2 nanoparticles may be applied to natural stones only by coating; rather than blending with material groundmass (e.g. cement, mortar or ceramic paste), this method allows using the whole quantity of TiO_2 that is activated by irradiation in the only effective surface layer. On the contrary, it can entail significant durability problems for the deposited films. In life service on the outdoor building surfaces, these films will be the direct interface with the environment and typically exposed to a variety of weathering processes, able to change the support characteristics and the stability of the coatings themselves. The main concerns of the coating's durability involve long run performance of the photocatalytic material surface and release of TiO_2 NPs into the environment. Potential problems including bioaccumulation, biotoxicity and biodegradability are related to NPs transfer and persistence in the environment. Investigation of these aspects is receiving increasing attention [37,38] and it appears relevant because production rates and use of engineered nanomaterials in many fields are expected to accelerate exponentially in the next few years, therefore, it is likely that increasingly amounts of these materials, typically having extreme smallness, strong mobility and reactivity could enter the environment. Although TiO_2 is well known as a non-toxic material, properties in the form of nanoparticles can be significantly changed in comparison with the material bulk. In recent years, some concerns have been progressively raised regarding potential health damage risk to humans, caused by the exposure to nanometric-sized TiO_2 particles. In this regard, adverse biological effects have been recorded by experimental toxicological studies on laboratory animals [39–43], so that loss of nano- TiO_2 from material surfaces deserves attention prior to large scale applications in the context of the building heritage. It has been recorded in natural weathering conditions from painted external façades [44]. Recent attempts have been made to evaluate the resistance of titania layers on the substrate in laboratory condition by means of tests simulating the effect of weathering factors, such as wind, water, light irradiation, etc. [45–51]. Some studies report quantitative evaluation of release of TiO_2 nanoparticles from coatings promoted by flowing of water and solutions containing environmental compounds such as humic acid and/or NaCl [52], as well as under wearing conditions [53]. Hsu & Chein [54] have recorded TiO_2 loss under rubbing and they have found that removed amounts may be influenced by previous exposure to UV, denoting a weakening of the film adhesion due to light irradiation. More often, the impact of ageing on the long run photocatalytic performances of the material surface has been investigated and a decrease of either self-cleaning abilities or abatement rates of NO_x have been recorded under various test conditions [52,55–57]. Substrate plays a role on the coating stability [53,54] and photocatalytic

performances [16,34,58] as well, which both can influence the properties of the coated surface in the long run. In this regard, limited information on long term behaviour of coatings applied to natural stone substrates has been so far achieved [59–62] and there is a current need of a better understanding of their durability issues in relation to different stone types, which may exhibit intrinsic characteristics in a wide range.

In this paper, TiO_2 coatings applied on a compact and a soft limestone, which differ in roughness, porosity and cohesion features, were investigated on their resistance. In the absence of standard procedures for the evaluation of adhesion of nano-structured coatings on the stone supports, a peeling and a water impact test were performed. These were aimed at simulating the mechanical effects of human touch and real rain. The latter is among the most probable and ubiquitous deterioration factors affecting the whole outside building façades and it may have in primis an effect on the durability of the surface coatings, depending on their anchorage to the stone supports. The film loss from the stone surface was evaluated by qualitative-quantitative ESEM-EDS analyses. The effect on the photocatalytic performances of the coated stones in terms of self-cleaning ability was assessed through a photodegradation test of Rhodamine B, which was performed before and after the durability tests.

2. Experimental

2.1. Materials and coating application

Two sols, water and alcohol based, having different concentrations of TiO_2 , were used for the stone coating, in order to compare the characteristics of the films issuing on the stone surfaces and photocatalytic properties and anchorage to the substrates. They were synthesized through sol-gel and hydrothermal treatment, starting from tetrapropyl orthotitanate (TPOT) as titanium dioxide precursor. The water-based TiO_2 suspension (1 wt %), denoted as TAQ1, was prepared following the procedure described in Ref. [63]. Briefly, required amount of TPOT (Sigma-Aldrich, 97%) was dissolved in water-oxalic acid (Sigma-Aldrich) mixture by drop wise adding TPOT in acidified water followed by heating at 80 °C for 2 h. Clear sols were obtained after the hydrolysis-condensation reactions; then they were kept inside an autoclave at 125 °C for 30 min while maintaining a pressure of 2 bar. After hydrothermal treatment, white suspensions of TiO_2 nanocrystals were obtained. The alcoholic solution (TAL2) with a TiO_2 content of 2 wt % was prepared by mixing TPOT in alcohol (80% v/v of propanol and 20% v/v of butanol ethanol) containing HCl followed by hydrothermal treatment at 125 °C for 30 min (pressure 2 bar), which yielded a white precipitate of TiO_2 nanocrystals, as in the previous case. Both suspensions were stirred continuously using magnetic stirrer prior to coating deposition.

Crystalline phases of the TiO_2 powders (Fig. 1) obtained by drying the suspensions at 60 °C in an oven, as determined by X-ray diffraction (XRD) on a Rigaku Ultima X-ray diffractometer ($\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$); 40 kV/30 mA; step size of 0.02°), in the case of TAQ1 sol consist of mainly anatase and rutile, with a little amount of brookite. TAL2 alcoholic suspension mainly contains anatase along with brookite and a slight amount of rutile.

Two calcareous stones (Trani stone and Lecce stone, hereafter indicated as PT and PL, respectively) with different microstructures were selected for the application of the TiO_2 coatings. Very different porosity features and roughness of the two stones have been reported in a previous study [64]. Briefly, PT stone is a compact limestone made of detritic grains and fossil fragments; it is very well cemented by a calcitic cement that almost completely fills the fine interparticle porosity. PL stone is a soft limestone made of

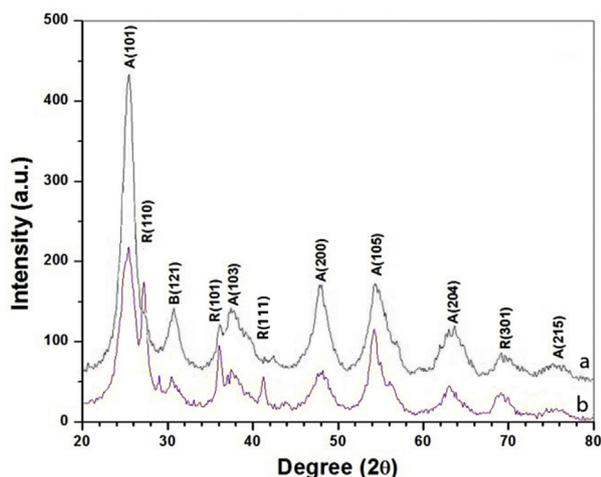


Fig. 1. XRD spectra of TAL2 (a) and TAQ1 (b) titania nanopowders. Corresponding *hkl* planes of anatase, rutile and brookite phases are indicated.

highly packed fossil remains within a fine calcareous groundmass; it is poorly cemented by small amounts of microcrystalline calcitic cement. Porosity of PT stone, as measured by Mercury Intrusion Porosimetry, is low (2%); it is made of very small pores, with the largest fraction (90%) of the pore radii lying between 0.007 and 0.05 μm . PL stone has a very high porosity (42%), which consists of larger pore sizes than PT stone. They lie mostly between radii of 0.3 and 10 μm (around 80%) with a distribution tail between 0.3 and 0.005 μm (20%). PL stone has typically a notably higher surface roughness than PT stone.

The titania sols were sprayed on stone specimens measuring $5 \times 5 \times 1$ cm by means of a H.V.L.P. (High Volume – Low Pressure, AKOKA Model H2000A) spray gun with 1.00 mm diameter nozzle, operating at a pressure of 2 bar. The sol was applied only onto one of the largest faces of each sample (i.e., that measuring 5×5 cm). The spray was directed perpendicularly to the stone surface, placed on a support inclined of 45° , from a distance of about 10 cm. During the coating, a temperature of 23 ± 2 $^\circ\text{C}$ and a relative humidity (R.H.) of $50 \pm 5\%$ were measured. The amounts of the sols applied were determined by measuring the weight of the samples before and immediately after the coating. For the PT samples, 3.5 mg/cm^2 of TiO_2 sol were applied; twice this quantity was applied for the PL specimens. The used quantities were found to vary among the samples between 7 and 18%. The applied sols correspond to TiO_2 loadings of 0.035 mg/cm^2 and 0.070 mg/cm^2 for TAQ1 and twice these quantities for TAL2, on PT and PL stones, respectively. Then the samples were dried in a controlled laboratory environment (23 ± 2 $^\circ\text{C}$ and $50 \pm 5\%$ R.H.) and stored in dark conditions.

2.2. Durability tests

A first evaluation of the anchorage of the films obtained on the stone surface was made through the “Scotch Tape test” [65]. It is a peeling test used for evaluating the surface cohesion of brittle and quasi-brittle materials, mainly mortars and stones. The test was performed on an area of 15×50 mm of the coated stone surface, by using a commercial bi-adhesive tape (Comet –TESA) 15 mm in width. One side of the tape was fixed on graph paper and strips, 6 cm length, were cut; the protection cover was removed and the strip was weighed on the analytical balance (± 0.1 mg precision). Then, it was stuck to the surface and smoothed with gentle finger pressure; after about 15 s, it was removed by pulling with a rapid and constant action at an angle of 90° . Finally, it was weighed in

order to determine the amount of detached material as the difference between the weight of the tape after removal from the surface and the weight of the clean tape before the application. The test was repeated 3 times on the same surface area, each time using new strips.

After peeling, the samples underwent a water impact test, to study the resistance of the coatings under a stronger mechanical action. A water jet having a diameter of 1 cm was sprayed on the specimen surface at a pressure of 0.2 bar from a distance of 50 cm; tap water was used. The specimen was placed horizontally and impacted by a perpendicular jet on a surface area of approximately 4 cm^2 . The test was carried out for 10 min; then it was stopped, as the erosion of the PL stone surface was observed. The total volume of water applied was 80 L.

2.3. ESEM-EDS analyses

Coupled Environmental Scanning Electron Microscopy (ESEM, Mod. XL30, FEI Company) and Energy-Dispersive X-ray spectroscopy (EDS) were used to investigate the morphology of the coatings and to detect the presence and distribution of Ti on the stone surface. Comparative ESEM observations and qualitative/quantitative analyses of Ti by EDS were performed before and after the durability tests, to study the effect of the applied mechanical actions on the coated stone surface.

Morphological and elemental analyses were performed on the samples without metallisation, in “low vacuum” mode, using a pressure of 0.6 Torr and a beam accelerating voltage of 25 kV. Both secondary (GSE) and backscattered (BSE) electron detectors were used. Distribution maps of Ti were acquired for each specimen via EDS using the EDAX Silicon Drift Detector (SDD) and they were analysed using the Genesis Spectrum software. Data were collected in Live Spectrum Mapping mode, which rasters frame after frame over the entire map area storing the entire spectral information, while updating the images and the cumulated spectrum. After data collection, the entire spectrum either at a selected point in the image or for the overall investigated area, can be retrieved; compositional maps can be built, as well. Acquisition was made on a sample area of $900 \times 700 \mu\text{m}^2$ (map resolution 512×400 , dwell 400 μs , frame 256).

2.4. Photo-degradation test of Rhodamine B

Photocatalytic activity of the coatings as self-cleaning photo-induced ability was evaluated by the photo-degradation test of Rhodamine B (RhB).

The test was performed on the samples before and after peeling and water impact tests and results were compared, to assess any changes of the photocatalytic effectiveness of the coatings on the stone surface.

A RhB aqueous solution (dye concentration = 0.05 g/l) was spread on both the uncoated and the coated surfaces; 63 mg/cm^2 of dye solution were applied on the porous stone, while 24 mg/cm^2 were used for the compact stone. After the drying (24 h in laboratory at 23 ± 2 $^\circ\text{C}$ and $50 \pm 5\%$ R.H.), colour measurements were carried out [66] by using a CR 300 Chroma Meter colorimeter (Minolta, Tokyo, Japan); five measurements were performed on each sample. The colorimeter was recalibrated to a calibration plate at the start of each session of 5 measurements. Colour characteristics were referred to the CIELab space, which expresses colours through the parameters L^* , a^* , and b^* , representing brightness and the red/green and yellow/blue chromatic intensities, respectively. Then, the samples were exposed to light using a solar simulator Solarbox 1500e R.H. (Erichsen Instruments). The radiation source was a Xenon lamp (1500 W power), located in the upper part of the

exposure chamber, in the axis of a parabolic mirror that guarantee irradiation uniformity. A soda-lime glass filter ensured irradiation in the range 275–825 nm, simulating the outdoor exposure. Light irradiance and temperature were set at 450 W/m² and 30 °C, respectively. These parameters were automatically monitored and controlled by a B.S.T. (Black Standard Thermometer) placed near the samples. Colour measurements were performed at different time spans (up to 450 min of irradiation) during the test in order to monitor the photocatalytic decomposition over time. Due to the red colour of RhB, parameter a^* evolution was used to control the photodegradation activity in terms of self-cleaning efficiency. The latter was expressed as percentage of discoloration (D) over time and it was calculated as:

$$D = \frac{|(a^*_{0} - a^*_{t})|}{|(a^*_{0} - a^*_{0})|} \times 100$$

where a^*_{0} and a^*_{t} are the values measured at the beginning of the test and at time t of irradiation, respectively; a^* is the value obtained by colour measurements before the application of the RhB solution.

3. Results and discussion

3.1. Coating resistance to peeling and water impact tests

The ESEM images in Fig. 2 show the surface microstructure of the uncoated stones. PT stone has tightly closed structure, with well-interlocked components and almost absent intergranular discontinuities. PL exhibits a microstructure consisting of detrital grains with high protrusion from the surface and low contacts among them, which give raise to higher roughness of the surface compared to PT stone [64]. Different coatings morphologies were obtained from the application of the two TiO₂ sols on the stone surfaces. TAL2 solution yielded clearly visible coatings, which masked the original surface morphology of both the stones (Fig. 3a, b). Due to the accumulation of TiO₂, high cracking was observed, leading to discontinuous films made of thick microscales, mostly having no contact points among them. Very often, the scales showed raised edges, with low anchorage to the stone support. Conformable coatings issued from the use of the TAQ1 dispersion (Fig. 3c, d), leaving unchanged the surface morphology of the stones. On both the substrates, no morphological evidence of these coatings was found, but the presence of Ti on the stone surface was detected by EDS analyses (Fig. 4). Therefore, considering that the TiO₂ content in TAL2 was twice the amount in TAQ1, the coating aspect seems affected by the TiO₂ loading.

Both peeling and water impact test showed that great loss of the films from the surface of the stones took place mainly when they were fissured, while continuity of the film accounted for a better anchorage at the stone surface.

The evaluation of the effect of peeling test is based on the weight measurements of the loss material; these failed in the case of the films under study, as the amounts of TiO₂ lost from the stone surface were found comparable to the measurement error. The effect of the peeling was visible by ESEM on the surface of both the stones coated with the TAL2 sol, where it resulted in a large removal of the fissured films. Coating fragments were almost completely lost from the surface of PT stone (Fig. 5); they were partially removed from the surface of PL stone (Fig. 6a, b). EDS distribution maps showed Ti still remained in higher concentrations only in some points on the surface of PT stone after the peeling (Fig. 7a); in the case of PL stone a strongly heterogeneous distribution of Ti on the surface was detected, with high concentrations corresponding to the film fragments, which were still widely present (Fig. 7b). It seems that the higher roughness of the PL surface better preserves the film between the protruding grains against the peeling action.

Checking of the peeling effect by ESEM observation was not possible in the case of TAQ1 films, as these coatings had no morphological evidence on both the stones since just after the deposition. Ti distribution, as mapped by the EDS analysis (Fig. 7c, d), showed a homogeneous presence on both the stone surfaces, with only some high concentration records in small points of the PT stone surface.

Ti/Ca ratios measured on the surface of the stones are reported in Table 1. In spite of the higher initial loading, Ti amount recorded on the surface of PT stone after peeling was lower for TAL2 than TAQ1 film, with Ti/Ca values of 3.26 and 8.84, respectively. These results are coherent with the significant loss of fragments affecting the cracked film and they evidence that the uniform film was able to preserve larger amounts of Ti on the stone surface. Conversely, Ti/Ca ratio notably decreased after peeling, but still remained higher on the surface of PL stone coated with TAL2 sol (14.19) compared to TAQ1 (9.11), in agreement with the lower loss of the fissured film, which survived to the peeling in a large extent, as it was previously evidenced.

After the water impact test, variations of the Ti distribution on the stone surfaces coated with TAL2 sol were clearly evident in the EDS maps. The reduction of Ti accumulation (Fig. 7a1, b1) showed that further detachment of the fissured fragments occurred. This failure gave the main contribution to the film loss, accounting for the different decreases of Ti/Ca ratios on the stone surface. The entity of the decrease was small for PT stone and higher for PL stone (Table 1), but also under the action of the water jet, the fissured film still survived on the surface of PL stone in wide amounts. It was observed that water impact on the soft PL limestone caused the removal of some portions of the coated stone layers (Fig. 6c), so that in this case the durability of the film resulted also related to the durability of the stone itself. This effect was not observed on the surface of the PT stone (Fig. 8). Indeed, PL is a friable calcarenite, due to the poor cementation of the detrital grains, which in

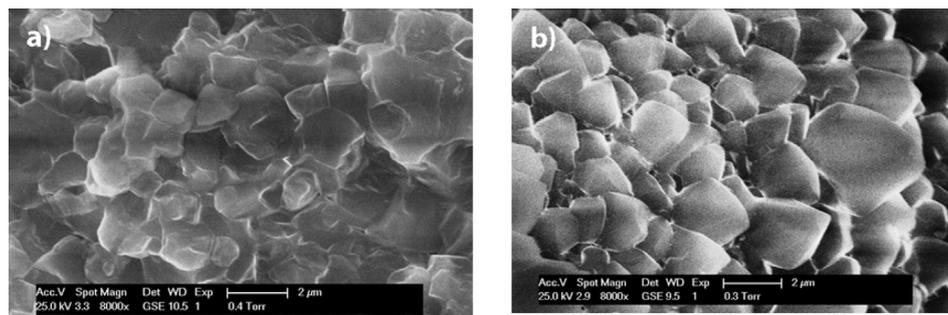


Fig. 2. ESEM images of the uncoated surface of the stones: a) PT stone; b) PL stone.

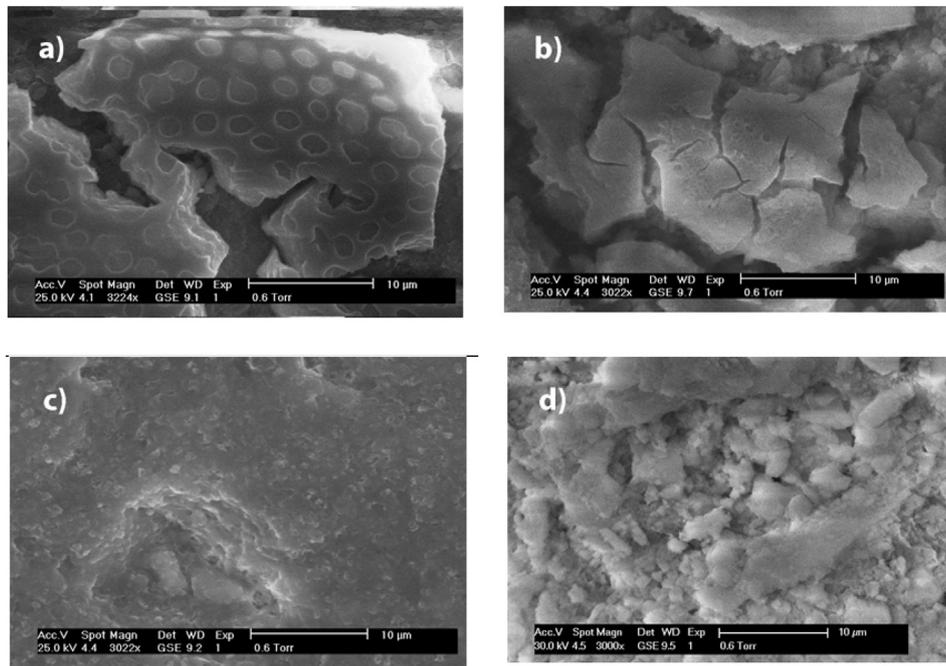


Fig. 3. ESEM images of the coated stone surfaces: a) and b) TAL2 film on PT and PL stones, respectively; c) and d) TAQ1 film on PT and PL stones, respectively.

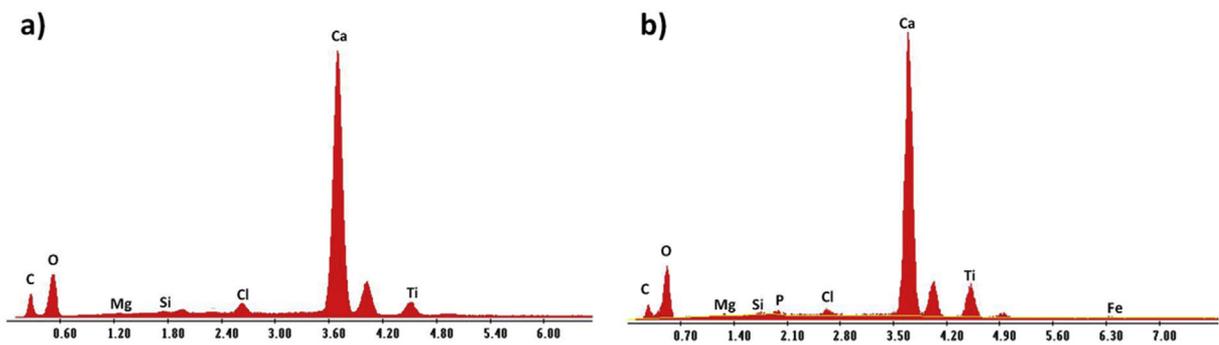


Fig. 4. EDS spectra on the surface of the stones coated with TAQ1: a) PT stone; b) PL stone.

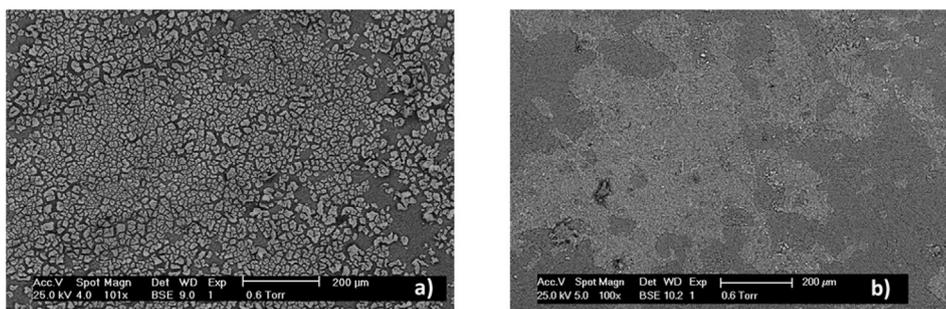


Fig. 5. TAL2 film on the surface of PT stone: a) before peeling; b) after peeling.

weathering conditions typically manifests a significant material powdering and loss from the exposed surface [67].

As reported in Table 1, in the case of TAQ1 films the decrease of Ti/Ca ratio after peeling was lower on the surface of the PL stone than PT stone. Good stability of these films under the water impact test was found on both the stones (Fig. 7c1, d1). After the test, Ti/Ca ratio was almost unchanged on the coated PL stone, while it slightly

decreased (from 8.84 to 7.52) on the surface of the compact PT limestone. On both the stones, Ti survived in higher amounts than in the TAL2 residual films.

With reference to the substrates, the results of both the tests pointed out a lower adhesion of the films on the surface of PT stone compared to PL stone, also in the case of the continuous and uniform TAQ1 coating. Lower roughness and porosity of the compact

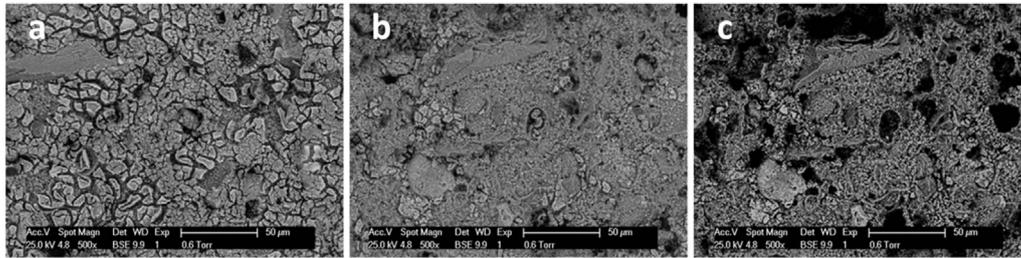


Fig. 6. TAL2 film on the surface of PL stone: a) before peeling; b) after peeling; c) after water impact test, with evidence of black cavities due to erosion of the stone surface.

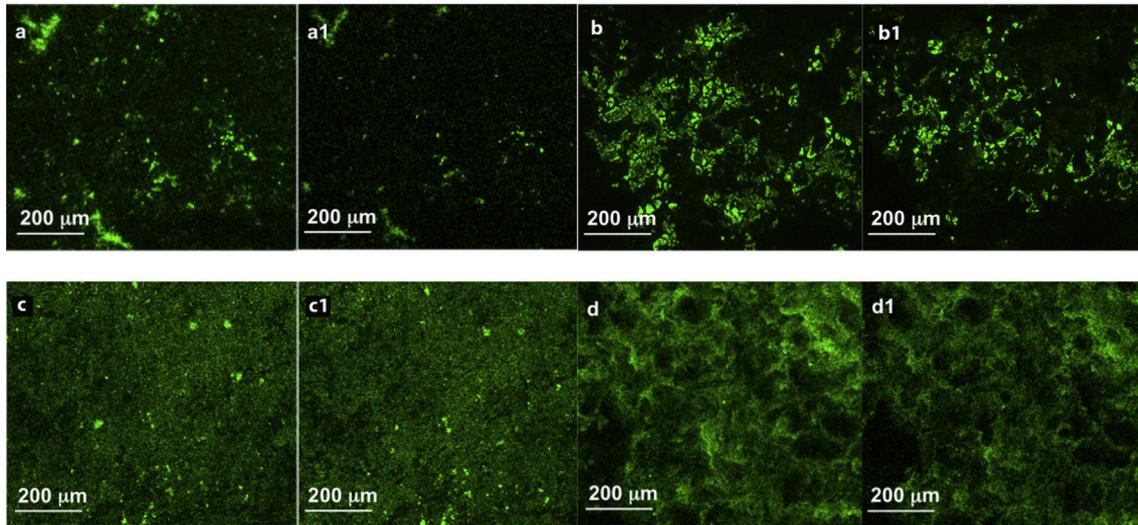


Fig. 7. Distribution maps of Ti on the stone surface. TAL2 film on PT after peeling (a) and after (a1) the water impact test; TAL2 film on PL after peeling (b) and after the water impact test (b1); TAQ1 film on PT after peeling (c) and after the water impact test (c1); TAQ1 film on PL before (d) and after the water impact test (d1) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Table 1
Ti/Ca ratios measured on the stone surface.

	PT stone			PL stone		
	Before peeling	After peeling and before water impact test	After peeling and water impact test	Before peeling	After peeling and before water impact test	After peeling and water impact test
Ti/Ca (TAL2 coating)	24.71	3.26	1.52	29.97	14.19	7.3
Ti/Ca (TAQ1coating)	11.42	8.84	7.52	10.12	9.11	9.00

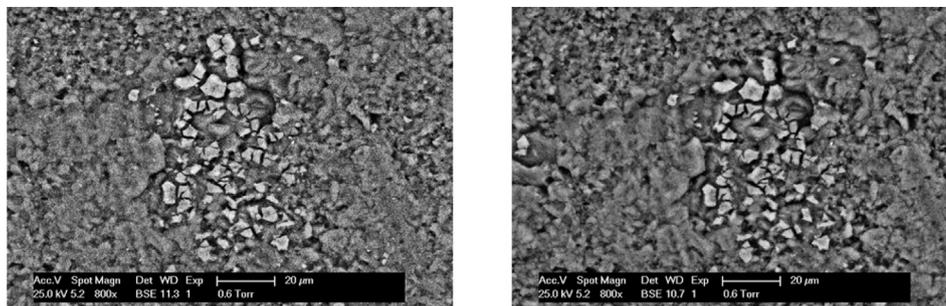


Fig. 8. Detail of the TAL2 film on the surface of PT stone after peeling: a) before water impact; b) after water impact.

limestone seem to account for a lower retention of TiO₂ nanoparticles, according to the findings obtained on cementitious

materials [16,53,58].

3.2. Photocatalytic activity of the coated surface

Photodegradation activity of the uncoated and coated stones, in terms of percent of decomposition of RhB (D %), is reported in Fig. 9, as a function of irradiation time. Before the durability tests, all the coated stones exhibited high photodegradation efficiency, with $D \geq 90\%$ at the end of the test (7.5 h); to the naked eye observation, the applied RhB almost completely disappeared from the sample surfaces (Fig. 10). As commonly known [68], the degradation of RhB under light exposure occurred, although to a low extent, even in absence of self-cleaning coatings.

Photodegradation efficiency reflected good self-cleaning abilities of the coated stones regardless of the TiO_2 amounts deposited on their surfaces with the two sols. In fact, in previous studies on cementitious materials, a parallel trend of RhB discoloration under halogen lamp radiation (simulating outdoor exposure) irrespective of TiO_2 load added to the paste [34] has been reported. Photoactivity of titania coatings has been proved to have close dependence on the availability of active sites with direct exposure to the light rather than total titania amounts [69].

The obtained results also highlight that the self-cleaning action can easily start also upon a short exposure to the sunlight. The highest decomposition rate was recorded at the early stages of irradiation; a significant degree of RhB degradation was measured already after 15 min of irradiation, while 2 h were sufficient to exceed 70% of degradation on most of the treated surfaces.

After peeling and water impact tests, except for the TAL2 coating on PT stone, the final photodegradation efficiency was almost unchanged if compared to the values recorded just after the deposition of the films (Fig. 9) and no evidence of residual Rhodamine B appeared on the sample surfaces (Fig. 10). Nonetheless, a small decrease of the kinetics of decomposition of the Rhodamine B was recorded. The photocatalytic effectiveness was well preserved also on those PL stone samples coated with TAL2 where a loss of stone layers from the surface was observed, thus meaning that the residual film was able to provide almost unchanged photocatalytic properties to the stone surface. This suggests that photocatalytic

activity was still supplied by TiO_2 NPs retained under the surface, according to their penetration within the stone [64]. On the contrary, photodegradation ability of the coating obtained from the TAL2 sol on PT stone, showed significant differences before and after the durability tests. The photodecomposition rate of RhB at the end of test was 70% and a significant decrease in the kinetics of the photodegradation process was observed (Fig. 9). Residual undegraded Rhodamine B was clearly visible to the naked eye on the sample surface (Fig. 10). The reduced photocatalytic performances of the coated stone suggest that a decrease of the effective photoactive surface likely occurred. Being the photocatalytic activity dependent on the presence/absence of photoactive sites on the overall surface, some areas with a complete removal of titania may have been produced by the coating adhesion failure, resulting in a reduced extent of the residual film on the stone.

4. Conclusions

Durability of nanostructured stone coatings obtained by the application of colloidal suspensions of Titanium dioxide synthesized by sol-gel and hydrothermal process, was investigated on the surface of two limestones.

Resistance of the coatings to peeling and water impact laboratory tests was evaluated.

The study highlighted that stability of photocatalytic TiO_2 coatings in relation to large-scale application to the stone surfaces in outdoor conditions deserves great attention, as different issues in terms of either film adhesion or long lasting photocatalytic effectiveness of the coated surface can be obtained, depending on the inherent characteristics of both coatings and substrates.

A better resistance was found for conformable and crack-free films, showing a good anchorage to both the stone supports, compared to the films affected by fissuring. Almost unchanged Ti/Ca ratios and self-cleaning efficiencies, as measured on the coated surface by EDS analysis and by the rate of photodecomposition of Rhodamine B, respectively, proved a good preservation of these films. Large adhesion failures and noticeable

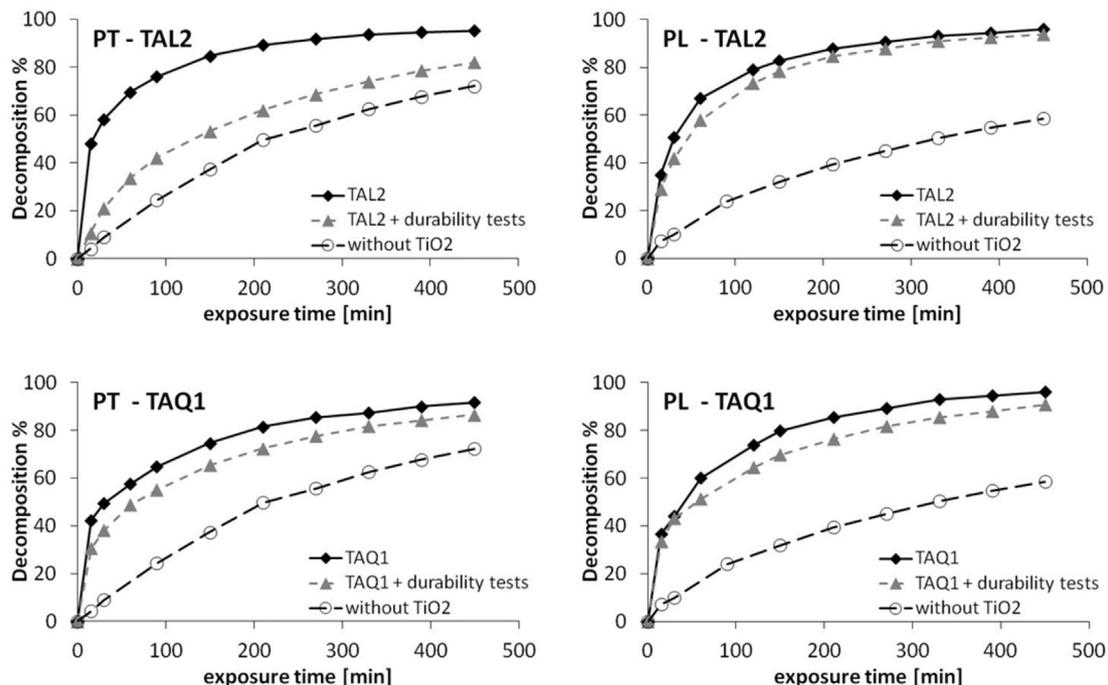


Fig. 9. Rates of decomposition of Rhodamine B before and after durability (peeling and water impact) tests.

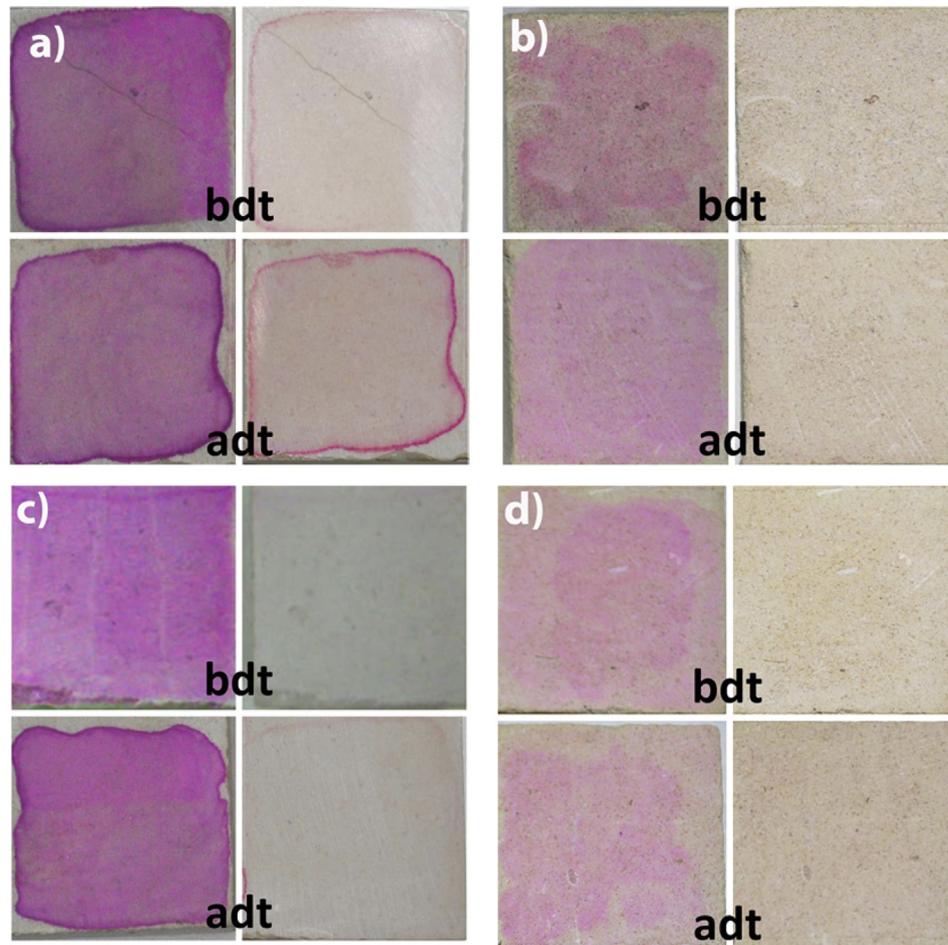


Fig. 10. Discolouring of Rhodamine B on the surface of the samples before (bdt) and after (adt) the durability tests. a) PT - TAL2 coating; b) PL - TAL2 coating; c) PT - TAQ1 coating; d) PL - TAQ1 coating (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

decrease of the Ti amounts were recorded when coatings were affected by cracking coming from the accumulation of titania applied in high amounts. The fissured coating showed a very low adhesion to the surface of the compact limestone, where it was mostly lost under the slight action of the peeling. In that case a reduced self-cleaning ability was recorded after the durability tests, denoting a decrease of the overall extent of the photocatalytically active surface because of a complete removal of TiO₂ NPs from some surface areas. Higher surface roughness of the soft limestone compared to the compact limestone accounts for the better adhesion of both fissured and crack free films to the substrate. Nonetheless, it was found that friability of this stone had an adverse role on the coating preservation; some erosion of the outer coated stone layers under the mechanical action of the water jet occurred during the test, but good photocatalytic effectiveness was still provided by nanoparticles retained under the surface.

Finally, the study highlight that great attention should be paid to the coating morphology, in order to obtain optimal films for large-scale applications on building surfaces. The very low adhesion of fissured films observed on the compact limestone suggests that this is a basic aspect to be addressed, in order to minimize their loss into the environment. Long-term run of the coatings on this stone needs to be investigated by further tests for better assessing the effect of more prolonged weathering action, as well as by studying their performances from lab to the real scale.

Durability of the coatings on friable stones, such as the soft limestones in this study, can be compromised by the low durability of the supports themselves. In these cases, enhanced stone cohesion should be addressed to increase use duration of the photocatalytic surface and suitable multifunctional products combining photocatalytic properties of TiO₂ NPs and surface hardening effect improving resistance and durability of the stone surface layers could be effective at this purpose.

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