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Self-cleaning and de-polluting stone surfaces: TiO_2 nanoparticles for limestone

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HIGHLIGHTS

- Limestone is a building material largely used for urban architectural surfaces.
- A TiO_2-nanoparticle coating was tested on it.
- Compatibility, self-cleaning and de-polluting effects were assessed.
- Results showed good compatibility with limestone surface.
- Evident photocatalytic efficiency was also demonstrated.

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ABSTRACT

To evaluate the self-cleaning and de-polluting properties of a transparent titania coating, in this investigation a titanium dioxide based suspension was deposited by spray coating on travertine, a porous limestone largely used as building material. To assess compatibility with stone substrates, microstructure analysis, color and gloss measurements, static contact angle analysis and two different water absorption tests were carried out. Self-cleaning and de-polluting activities were assessed by the use of rhodamine B decoloration and NO_x degradation tests. The results showed good compatibility with stone surfaces and evident efficiency, allowing the use of titania coatings for real outdoor applications.

1. Introduction

Photocatalysis, that is the acceleration of chemical redox reactions thanks to the synergy of particular materials (usually semiconductor) and solar light, is one of the most promising tool for the handling of different problems in several areas of applied chemistry, including environmental science. In fact photocatalysis allows the photo-decomposition of both organic and inorganic polluting substances absorbed or deposited on photoactive surfaces by redox reactions induced by solar light.

Titanium dioxide (TiO_2) is one of the mostly used photocatalytic material in order to develop innovative materials and solutions in different fields: water and air purification, anti-bacterial and self-sterilizing surfaces, food industry, paintings, paper production, cosmetics and building materials [1–7]. In construction sector titanium dioxide has been used to realize self-cleaning treatments in a large number of building elements, as cement mortars, exterior tiles, paving blocks, glasses, paints, finishing coatings, road-blocks, concrete pavements [7–14]. Its widespread use is attributed to its main features: high catalysis efficiency, chemical stability, inexpensiveness, non-toxicity, compatibility with traditional construction materials [3–5,7].

Photocatalysis is not the only photochemical effect of TiO_2 activated by ultraviolet irradiation of solar light. Under UV exposure titanium dioxide becomes super-hydrophilic, thus decreasing water contact angle and creating an uniform water film on treated surfaces [1,2], preventing contact between external dirt and surfaces themselves.

The synergy of these two photo-induced properties (photocatalysis and super-hydrophilicity) is the base of self-cleaning ability of

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TiO_2 [7], since the formation of a water film over treated surfaces and the photocatalytic degradation of pollutants and external agents could make removal of degradation agents easier bringing to a real self-cleaning effect.

Titanium dioxide shows three different crystal structures: anatase, rutile and brookite. The photocatalytic efficiency of TiO_2 is greatly influenced by its structure: amorphous titania shows very little photoactivity while this property is much more evident in crystal form, especially for anatase nanocrystals. However, among the interesting properties of anatase nanoparticles, they are characterized by a mean diameter below the light wavelength and thus they are transparent if applied on a substrate or dispersed in a matrix. Nanostructured titania films over a solid surfaces can allow to obtain a transparent physical barrier to enhance the cleanibility of treated substrate without altering its aspect.

In this scenario, surface treatments can effectively improve the conservation, protection and maintenance of several types of stone surfaces and elements, since the action of many degradation agents begins from the outer layers of these surfaces. The development and application of transparent self-cleaning coatings could improve the preservation of the original aspect of treated elements, decreasing the deposition of pollutants and soiling on building surfaces and reducing the onset of external degradation processes due to soiling phenomena, thus limiting cleaning and maintenance actions [15–21].

The aim of this work was to evaluate the possible use of TiO_2-based coatings over architectural stone surfaces, analyzing both their efficiency and the effects induced to treated substrates by their properties. In order to establish efficiency and compatibility of titania coatings to preserve building stones, historical monuments, architectural and artistic stone elements, the travertine, a natural limestone, was selected as the reference substrate. Travertine is a porous carbonatic stone widely used in historical building and monuments in Europe and Mediterranean Basin and it is still one of the most frequently used stone material in modern architecture, especially for façades, flooring and external cladding [18,19].

Particular attention was paid in the estimation of the consequence of photo-induced hydrophilicity on treated substrate since, especially for treatment on porous materials, higher wettability could bring to higher water absorption, a potential source of damage for porous materials.

2. Experimental

2.1. Coating preparation

The used titania nanoparticles were developed in Ce.Ri.Col. (Colorobbia Research Centre, Colorobbia Italia), and were synthesized in water via polyol synthesis [22]. This method leads to oxide or metal inorganic nanoparticle suspensions, that are easier to manage and environmentally more friendly than a nanopowder. The titania content of the aqueous suspension was 6wt% with a mean particle size of 18 nm. Before application over limestone surfaces, the suspension was further diluted with demineralized water up to obtain a suspension with a TiO_2 content of 1% by weight.

Travertine prismatic elements ($8.0 \times 8.0 \times 1.5\ cm^3$) were prepared according to the dimensional requirements of selected tests to be performed [18,19].

TiO_2-based suspension was applied on travertine samples by spray coating obtaining two different treatments: single layer (C1) and three layers (C2) coatings. Application through spray coating was chosen due the simplicity and quickness of this method and its compatibility with stone surfaces and with other restoration techniques, an important prerequisite for application on Cultural Heritage [18–20].

During the air-brushing application, sample surfaces were kept at a distance of about 40 cm from the nozzle (diameter: 1.5 mm) of spray gun. Travertine surfaces were coated with 25 ml/m^2 (C1 treatment) or 70 ml/m^2 (C2 treatment) on average. After spray deposition, treated specimens were dried in a ventilated oven for 1 h at about 70 °C. This drying phase is not strictly necessary and can be avoided in real outdoor use on stone surfaces, since it simply accelerates the normal process of drying. Any other additional or subsequent thermal treatment was avoided [23,24], since it is not always possible to use thermal processes on outdoor building stones, both in the field of Cultural Heritage [16–19,25] and modern architectural surfaces.

2.2. Coating characterization

To evaluate the potential use of titania coatings on architectural elements and cladding made by travertine, it is necessary to verify the fulfilment of several requirements: TiO_2-based treatments must show a real self-cleaning efficiency without altering the original aspect of substrates (especially in the field of Architectural Heritage) and causing adverse effects on preservation of stone elements due to possible physical and chemical changes on treated surfaces.

2.2.1. Microstructure analysis

Microstructure of both untreated and coated limestone surfaces was investigated by scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), using a FEI Quanta-200 instrument.

2.2.2. Aesthetical properties

Aesthetical changes of travertine due to the application of titania suspension were monitored by color [15,17,18,20,21,26,27] and gloss analyses [14,18,26,28]. The chromatic variations were measured in the CIELab color space [29] by a Konica Minolta CM-2600 d spectrophotometer. At least nine measurements were carried out on each stone sample, using five samples for each case [27]. Color difference ΔE^* [29] between two values was determined according to:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \quad (1)$$

The gloss was measured by the use of a Novo Gloss Trio apparatus (Rophoint Instruments, standard geometry for measurements: 60°), analyzing at least three specimens for each case and carrying out eight measurements for each sample. As for non-metallic paints and materials, measurement scale of gloss is between 0 (perfectly matt surface) and 100 gloss units (GUs). In the case of low gloss surfaces (60° specular gloss below 10 GUs), it is necessary to change the measurement angle to 85° [26,28]. Both color and gloss analyses were performed before and after deposition of titania suspension on stone surfaces.

2.2.3. Water absorption

In order to assess how the stone surface is modified by the deposited coatings, static water contact angle [15,17,19–21,26,30], capillary water absorption [17,19–21,26,31] and a specific surface water absorption [19] analyses were carried out. High wettability due to photo-induced hydrophilism of TiO_2 could bring to a great water absorption, a potential source of damage for porous stones.

Static contact angle (CA) test [30] was performed using an OCA 20 apparatus (DataPhysics Instrument GmbH, Filderstadt, Germany). Static CAs were determined using a drop volume of 5 μl, performing 15 measurements for each test sample on 3 uncoated samples and 2 specimens for each kind of different treatment (C1 and C2) [30]. The determination of static contact angles for porous and rough surfaces, such as that of travertine, is not simple and it is deeply influenced by surface irregularity, so the results should be carefully considered [19].

Original travertine samples ($8.0 \times 8.0 \times 1.5\ cm^3$) were divided by cut into 3 parts each (about $2.5 \times 8.0 \times 1.5\ cm^3$). Six samples for each treatment condition (untreated, C1, C2) were analyzed to assess water absorption by capillarity [31] and evaluate possible changes of wettability of treated surfaces. After cut, lateral surfaces of specimens were sealed in order to reduce water absorption from untreated faces of travertine during test, then stone samples were dried in a ventilated oven until reaching constant mass. It was assumed that constant mass is reached when the difference between two successive weighing at an interval of 24 h is not greater than 0.1% of the mass of the specimen. Travertine samples were placed in a vessel on a bedding layer saturated with demineralized water: treated samples were lying on coated side. The amounts of absorbed water at time t_i (s) were established by weighing and then denoted as absorbed mass per unit area Q_i (kg/m^2):

$$Q_i = (m_i - m_0)/A \quad (2)$$

where A is the area of the stone samples exposed to water (m^2). Capillary water absorption coefficient AC was defined as the slope of the linear section of the curve obtained plotting the mass change per area (Q_i) versus the square root of time ($t_i^{1/2}$) and was calculated by linear regression, using at least five successive aligned points. Because of test method it was not possible to expose test specimens to UV light.

Surface water absorption was evaluated by a specific test procedure [19]. Groups of three stone specimens (the same samples used for capillary water absorption test, $2.5 \times 8.0 \times 1.5\ cm^3$) were placed on a support inclined 10 degrees from the vertical plane and then wet by a settled amount of demineralised water sprayed every 2 min by the use of a manual nebulizer on the surface up to a total of 60 min. Absorbed water was measured by weighing after each spray and then denoted as Q_i (2). Total amount of water sprayed at the end of the test was about 50 ml for each group of three samples, the distance between samples and nebulizer nozzle was about 30 cm. Lateral surfaces were sealed as before. Three specimens were analyzed for each treatment condition (untreated, C1, C2). In the case of treated surfaces water was sprayed on coated face of specimen. The test was carried out with and without ultraviolet illumination (60 min long exposure, wavelength range: 325–390 nm, irradiance value: 20 W/m^2) to assess the consequences of possible photo-induced hydrophilicity due to titania.