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Photocatalytic hydroxyapatite-titania nanocomposites for preventive conservation of marble

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Abstract. Soiling of external surfaces is an increasing issue for conservation of architectural heritage. Providing architectural surfaces with self-cleaning ability is one of the most promising routes of preventive conservation. To this aim, several methods have been proposed in the literature, based on the use of photocatalytic TiO₂ nanoparticles, either directly applied onto the surfaces or incorporated in protective coatings. However, when nano-TiO₂ is directly applied onto architectural surfaces, the particles are easily removed by rain. When TiO₂ is incorporated in polymeric coatings, durability issues arise as well, because the photoactivity of TiO₂ nanoparticles can promote degradation of the polymer. Here, we present an innovative alternative method, based on combination of TiO₂ nanoparticles and hydroxyapatite (HAP). The incorporation of nano-TiO₂ into an HAP coating protects the nanoparticles from leaching by rain, thanks to the chemical bonding between TiO₂ and HAP, without diminishing their photoactivity. As a result, marble treated with HAP-TiO₂ composites exhibits high self-cleaning ability and high durability, with results superior to those achieved by direct application of nano-TiO₂ onto the surface, as frequently performed on site.

1. Introduction

Soiling of external surfaces by particulate matter present in the atmosphere is extremely important for cultural heritage conservation. To prevent soiling, the use of photocatalytic TiO₂ nanoparticles has been proposed, with the aim of providing existing surfaces with self-cleaning properties [1]. Two main routes have been pursued: (1) applying suspensions of TiO₂ nanoparticles directly onto the architectural surfaces, so that particles are retained on the surface after solvent evaporation; (2) incorporating TiO₂ nanoparticles into protective coatings. The first approach has the advantage of leading to high photocatalytic efficacy, because TiO₂ nanoparticles are directly exposed to solar radiation. However, because of the weak adhesion between the particles and the substrate, nano-TiO₂ directly applied onto historic surfaces is easily removed by rain [2]. This led to the second approach, i.e. incorporating the particles into coatings aimed at protecting them from leaching by rain. Coatings of various types have been proposed, including inorganic, organic and hybrid coatings. This approach has the advantage that particles are protected from leaching and mechanical strengthening can also be achieved by a single treatment. However, when organic matrices are used, the polymer binding the TiO₂ particles might be



deteriorated by exposure to UV radiation and might even undergo accelerated degradation caused by the photocatalytic activity of the particles themselves [3].

With the aim of developing photocatalytic composites with enhanced durability, in the present study we investigated the combination of nano-TiO₂ with hydroxyapatite (HAP, Ca₁₀(PO₄)₆(OH)₂). HAP coatings have been proposed for protection of marble from dissolution in rain, by formation of a superficial layer of HAP (having very low solubility) over calcite [4]. To form HAP, marble is treated by an aqueous solution of diammonium hydrogen phosphate (DAP, (NH₄)₂HPO₄) [5]. HAP-TiO₂ composites were here developed by introducing TiO₂ nano-particles into the DAP solution, so that particles are embedded by HAP formation. The photocatalytic activity and the resistance to simulated rain of such composites were evaluated and compared, on the one hand, to those of HAP alone and TiO₂ alone and, on the other hand, to a combined treatment simply involving sequential application of TiO₂ over an already formed HAP coating.

2. Materials and methods

2.1. Materials

Carrara marble was used for the tests, as this lithotype has been widely used in historic architecture and sculpture and because the issue of nano-TiO₂ leaching by rain is particularly relevant in the case of smooth surfaces such as marble. Moreover, the good efficacy and compatibility of the HAP-treatment on marble has been previously assessed [6,7]. Samples with 30×30×20 mm³ size were sawn from a slab supplied by Imbellone Michelangelo s.r.l. (Italy). Before any treatment, all the samples were preliminarily artificially weathered by heating in an oven at 400 °C for 1 hour, to reproduce the micro-cracking typically affecting naturally weathered marble [6]. Part of the samples was left untreated and used as reference, while the remaining samples were treated as described below.

2.2. Treatments

Samples subjected to the hydroxyapatite-treatment alone (labelled “HAP”) were treated by application of a 3 M aqueous solution of DAP (Sigma-Aldrich, assay ≥ 98%), applied by brush until apparent refusal (8 brush strokes). After curing for 48 hours wrapped in a plastic film, samples were rinsed with water and dried at room temperature. A limewater poultice was then applied, to further promote HAP formation and to remove unreacted DAP during drying [7]. Samples were finally rinsed with deionized water and dried at room temperature.

Samples subjected to the TiO₂-treatment alone (labelled “TiO₂”) were treated by application of a 2 wt% suspension of nano-TiO₂ in 80-20 wt% water-isopropanol, applied by a single brush stroke.

Samples subjected to the sequential application of the HAP and TiO₂ treatments (labelled “HAP then TiO₂”) were treated by applying the two single treatments described above, in sequence.

Samples subjected to the combined treatment (labelled “HAP with TiO₂”) were treated by application of a 3 M DAP solution also containing 1.5 wt% of the same suspension used for the “TiO₂” treatment. In this case, the treatment was applied until apparent refusal (8 brush strokes), and then the samples were subjected to application of the limewater poultice, as described above.

2.3. Characterization

The coating composition was analysed by Raman spectroscopy (Renishaw Raman Invia spectrometer, linked to a Leica DMLM optical microscope). In particular, the possible formation of Ti-O-P bonds in the “HAP with TiO₂” treatment was investigated.

The surface morphology was analysed by observing the samples with an environmental scanning electron microscope (FEI Quanta 200 FEG ESEM), after carbon coating. The microstructure of the “HAP” and “HAP with TiO₂” coatings was investigated by cutting a cross section using a focused ion beam SEM (FEI StrataTM DB 235 FIB), after carbon coating. In particular, the possible effect of TiO₂ particles on HAP crystallization was investigated.

The aesthetic compatibility of the coatings was evaluated by determining the colour change (ΔE^*) after treatment, calculated as $\Delta E^* = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2}$. The CIELAB colour parameters L^* (black÷white), a^* (red÷green) and b^* (yellow÷blue) were measured by an optical fibre spectrophotometer Ocean optics USB2000+ in reflective mode.

The photocatalytic activity of the coatings was evaluated by the methylene blue degradation test [1]. Samples were first stained by a drop of methylene blue solution (10 g/l) and the colour parameters were determined. After exposure for 2 hours to UV radiation (50 W, $\lambda=365$ nm, distance from the lamp to the samples of 20 cm), the colour parameters were measured again.

To evaluate the resistance to nano-TiO₂ leaching by rain, samples (previously not used for any other test) were subjected to dripping of deionized water at pH 5.6 onto a 9 cm² surface, by means of a custom-designed apparatus [8]. After dripping a volume of water corresponding to the amount of rain that falls in ~6 years in Bologna (Italy), samples were dried and then subjected to the methylene blue test, carried out as described above. To evaluate the TiO₂ leaching from the marble surface, the runoff water was collected and the Ti content was analysed by inductively coupled plasma optical emission spectrometry (ICP-OES), using a Horiba ULTIMA 2 spectrometer.

3. Results and discussion

3.1. Coating composition, microstructure and aesthetic compatibility

In the case of the single treatments and the sequential treatment, Raman spectroscopy detected bands ascribable to HAP (959, 594 and 434 cm⁻¹ [9]) and anatase (638, 520, 406 and 147 cm⁻¹ [11]), as expected (Figure 1). Alongside HAP, formation of octacalcium phosphate (OCP, C₈(PO₄)₆H₂·5H₂O) cannot be completely excluded, as the detected bands are also compatible with OCP [9]. In any case, OCP formation is not expected to negatively affect the coating performance, because OCP is much less soluble than calcite [4]. In the case of the “HAP with TiO₂” treatment, in addition to the HAP and TiO₂ bands, a new band appeared at 1007 cm⁻¹, which suggests formation of a Ti-O-P chemical bond [11]. Formation of such a bond is expected to guarantee good adhesion between the TiO₂ nanoparticles and the HAP coating, with a positive outcome in terms of durability to simulated rain.

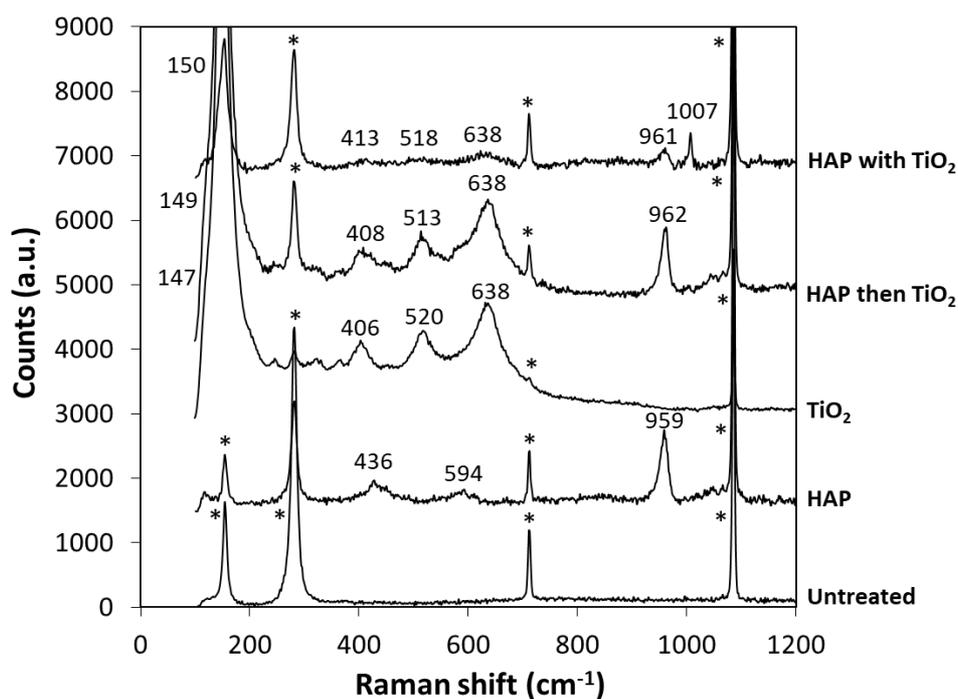


Figure 1. Raman spectra of untreated and treated samples. Calcite bands are indicated by a star.

The surface morphology of untreated and treated samples is illustrated in Figure 2. Although the coatings are all affected by diffused cracking (Figures 2-5), the “HAP with TiO₂” coating exhibits less cracking and apparently denser microstructure (Figures 2 and 6). This is thought to be a positive consequence of the presence of TiO₂ nanoparticles during HAP formation, because: (i) the particles might act as “seeds” during HAP crystallization [12]; (ii) the particles might limit shrinkage and cracking during drying (providing a similar action as they do in particle modified consolidants) [13]; (iii) the isopropanol contained in the TiO₂ suspension added to the DAP solution might favour HAP formation [14]. Accordingly, the FIB cross sections of the “HAP” and “HAP with TiO₂” coatings reveal that, for the latter treatment, a refined microstructure is present (Figure 2, dashed box).

In terms of aesthetic compatibility, all the treatments are suitable for application on white marble, because in no case did the colour change (ΔE^*) after treatment exceed the threshold commonly accepted for conservation treatments ($\Delta E^* = 5$ [13]) (Table 1).

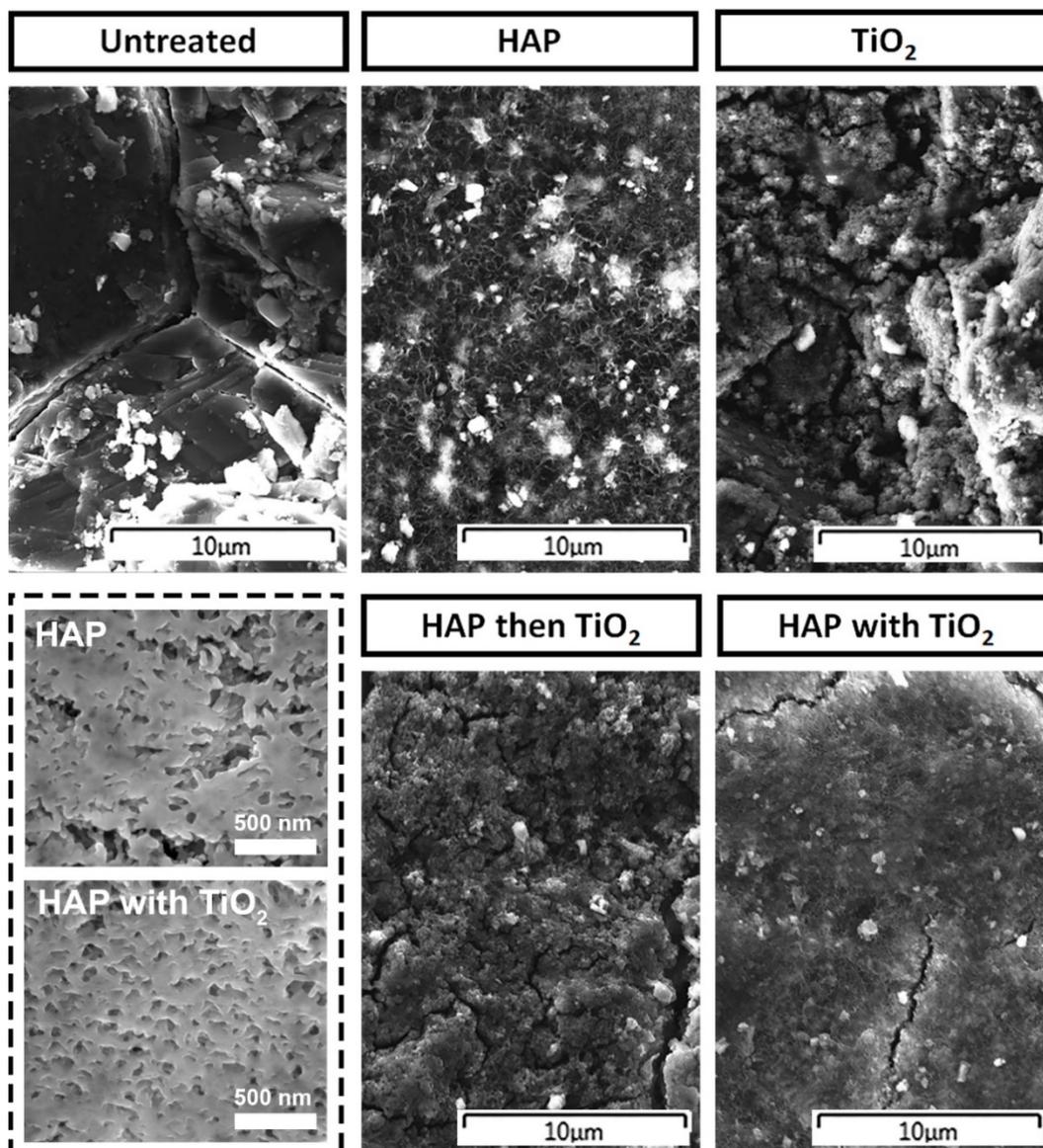


Figure 2. Surface morphology of untreated and treated samples and FIB cross sections of the “HAP” and “HAP with TiO₂” coatings (dashed box).

Table 1. Colour variation (ΔE^*) after treatment and after the methylene blue discoloration test, carried out before and after exposure of the samples to simulated rain.

Condition	Compatibility		Self-cleaning ability (degradation of methylene blue)	
	ΔE^* after treatment		ΔE^* pre-simulated rain	ΔE^* post-simulated rain
Untreated	-		1.3	1.6
HAP	2.2		4.9	3.4
TiO ₂	1.9		20.9	13.2
HAP then TiO ₂	1.2		20.7	17.1
HAP with TiO ₂	0.6		17.6	16.3

3.2. Photocatalytic ability

The results of the methylene blue test are reported in Table 1. Whereas the untreated reference exhibits very little discoloration and the “HAP” sample only limited self-cleaning ability, as expected, all the treatments containing TiO₂ exhibit high discoloration ability, fully comparable to values reported in the literature for alternative coatings [1]. In detail, the “TiO₂” and the “HAP then TiO₂” coatings provided the highest self-cleaning ability, consistent with the fact that high and comparable amounts of TiO₂ are present over the surface of the respective coatings (Figures 4 and 5, “PRE” condition). Notably, the self-cleaning ability of the “HAP with TiO₂” coating was a little lower (17.6 vs 20.7-20.9, Table 1), but still remarkable, considering that in this case the amount of TiO₂ detected on the surface is very low (0.1 vs 31.9-32.4 wt%, Figures 4-6, “PRE” condition). Such a low value is due to the low amount of nano-TiO₂ suspension added to the DAP solution (cf. § 2.2) and to the application of the limewater poultice at the end of the treatment (cf. § 2.2), which removed all loosely bonded particles.

3.3. Durability

After exposure to simulated rain, the self-cleaning ability of the various treatments was altered as reported in Table 1. Minor changes were observed in the case of the untreated reference and the “HAP” coating, as expected. The “TiO₂” coating experienced the highest reduction (-35%), as a consequence of abundant removal of TiO₂ nanoparticles from the sample surface. This is explained by SEM observation of the sample surface (Figure 4, “POST” condition), which reveals a drastic reduction in Ti content (from 31.9 to 1.1 wt%), and by ICP analysis of the runoff water, containing the highest amount of Ti (0.256 ppm).

The “HAP then TiO₂” coating exhibited a lower reduction in photocatalytic activity (-17%), even though the TiO₂ nanoparticles had been simply applied over the HAP coating, with no encapsulation in the coating and no apparent chemical bonding (Figure 1). Nonetheless, TiO₂ removal from the surface was minimal (Figure 5, “PRE” and “POST” conditions) and a much lower Ti content was detected in the runoff water, compared to the “TiO₂” coating (0.085 ppm). The scarce removal of particles in this coating and the consequent good residual self-cleaning ability are thought to be a consequence of the improved adhesion, although physical in nature, between the particles and the HAP surface. Compared to the marble surface, the flower-like morphology and the high specific surface area of HAP allow for better adhesion of the particles, which are better retained during exposure to simulated rain.

In the case of the “HAP with TiO₂” coating, the chemical bonding between the particles and the HAP coating ensured that almost no removal of TiO₂ occurred (Figure 6, “PRE” and “POST” conditions), with consequent very low decrease in photocatalytic activity (-7%) and very low amount of Ti detected in runoff water (0.025 ppm). These results point out the high potential of the composite coating obtained by incorporating nano-TiO₂ into HAP, characterized by high photocatalytic activity and high durability at the same time.

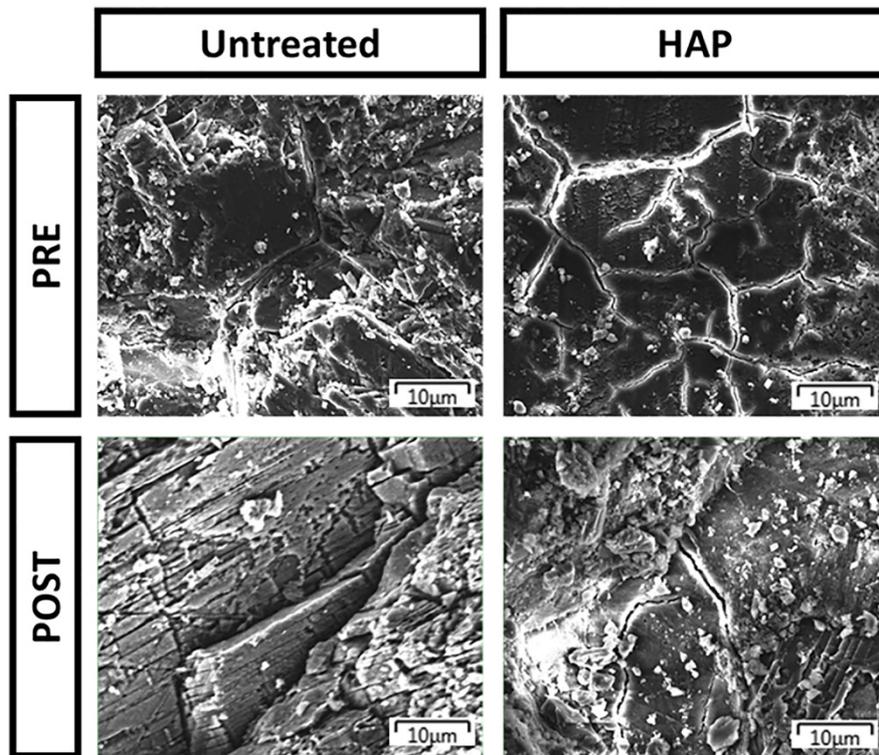


Figure 3. Surface morphology of untreated and “HAP” samples, before (PRE) and after (POST) exposure to simulated rain.

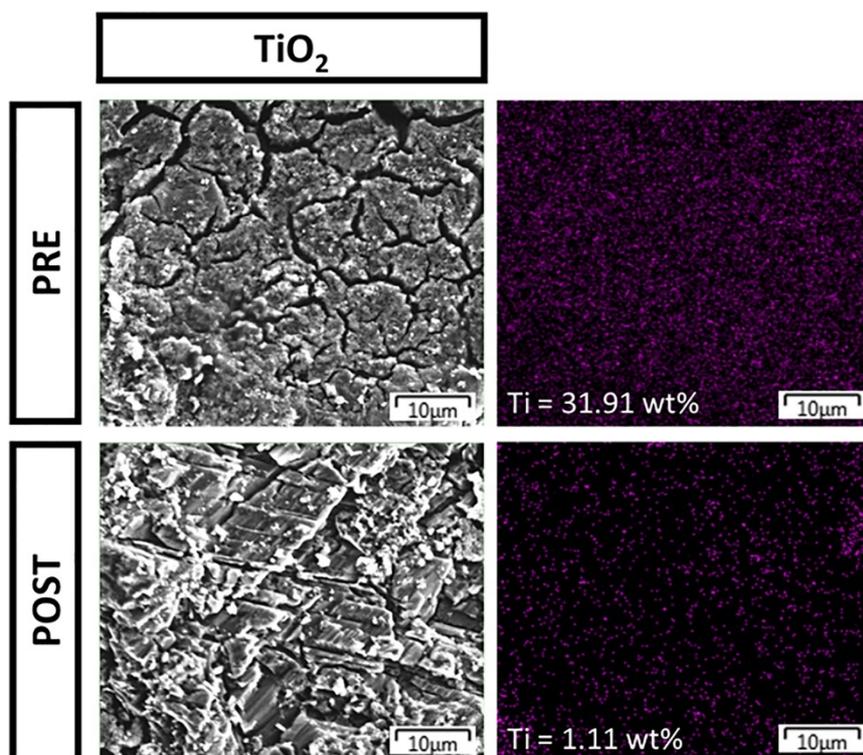


Figure 4. Surface morphology and EDS maps of “TiO₂” samples, before (PRE) and after (POST) exposure to simulated rain.

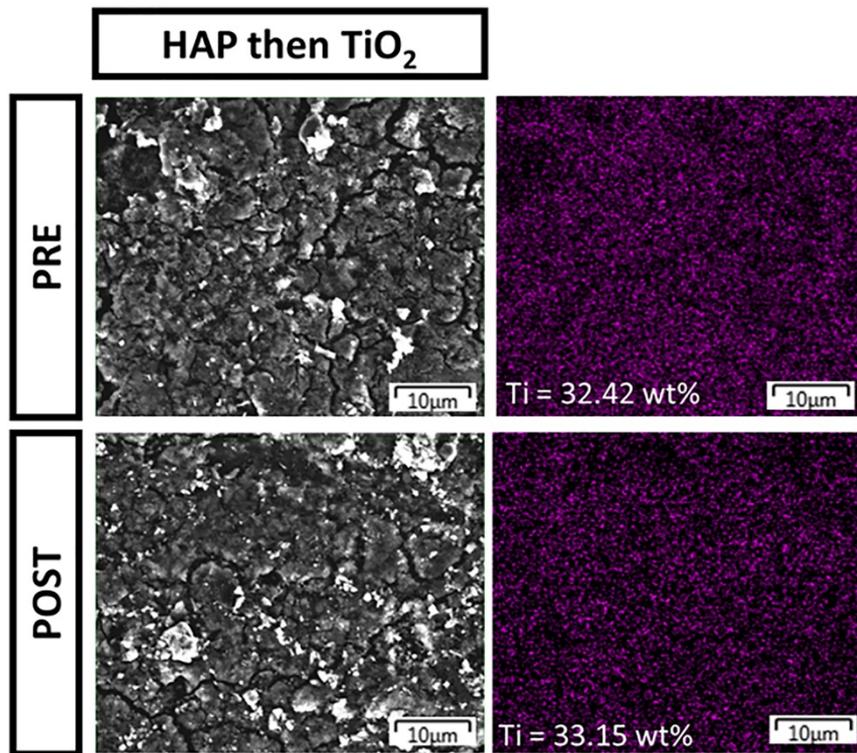


Figure 5. Surface morphology and EDS maps of “HAP then TiO₂” samples, before (PRE) and after (POST) exposure to simulated rain.

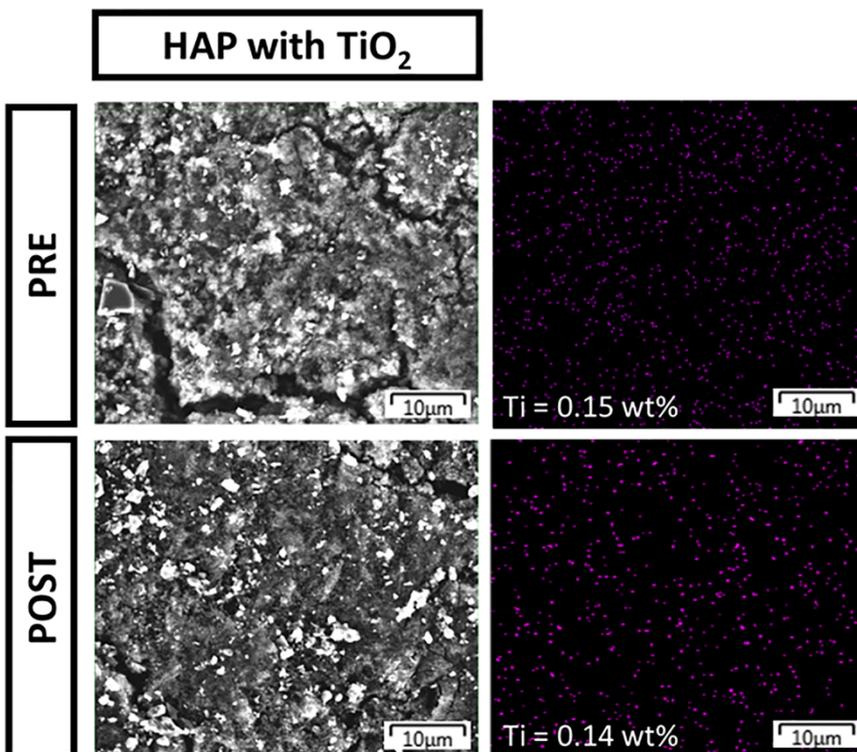


Figure 6. Surface morphology and EDS maps of “HAP with TiO₂” samples, before (PRE) and after (POST) exposure to simulated rain.

4. Conclusions

In this study, we investigated the combination of TiO₂ nanoparticles and hydroxyapatite as an innovative route to obtain coatings with high self-cleaning ability and high resistance to TiO₂ leaching by rain. The HAP-TiO₂ composite outperformed simple application of TiO₂ nanoparticles directly onto marble surface, which is currently the most common practice in the field. Very good results were obtained also in the case of sequential application of nano-TiO₂ over an already formed HAP coating, because the high specific surface area of HAP allows for a better physical adhesion between the particles and the substrate, compared to calcite. Although results of mechanical tests were not reported here for brevity's sake, both the combined and the sequential treatments were also able to fully restore the cohesion of artificially weathered marble, which is a further important aspect. Because the HAP-based treatment is attracting increasing attention and it has been explored for a variety of different substrates (from other stone types to concrete), the development of HAP-TiO₂ composites looks like a very promising route for preventive conservation of architectural surfaces in the built environment.

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