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Contents

Active photocatalytic-superhydrophobic coating with TiO_2/ZnO nano-heterostructures for lime mortars

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Abstract

Active coatings to be applied onto hardened surfaces of lime rendering and masonry mortars and stones of the Built Heritage were developed. Nano-heterostructures of TiO_2/ZnO (50:50 and 10:90) were obtained by Flame Spray Pyrolysis as photocatalytic agents with expanded sensitivity towards solar light, instead of the restricted UV dependence of the pure TiO_2 or ZnO. A superhydrophobic medium was simultaneously prepared and photocatalytic nanoparticles were added to obtain the coatings. The active products were expected to prevent the water absorption of the substrates and the subsequent degradation effects as well as to allow the stones and mortars to act as self-cleaning materials, reducing the dirt deposition and the biological colonization. Dispersions were applied onto the surface of lime mortars and siliceous stone. Measurements of the photocatalytic oxidation activity of the coatings were carried out by means of the NO degradation, showing a very good efficiency of the nanoparticles even at long term tests (values of NO oxidation of ca. 35%). Water contact angle assessment evidenced a strong hydrophobization of the treated surfaces, with WCA values higher than 140°. The results proved the synergistic effect of these coatings with respect to the durability of the treated substrates, giving rise to a promising way of preventive conservation for building materials of the Cultural Heritage.

Introduction

In terms of preventive conservation, the use of water-repellent and biocide materials can be useful for keeping clean and safe Built Heritage for long time [1,2]. Active coatings could be applied onto the building materials (pre-existent and new repair components as well) to prevent the water access, the accumulation of dirt deposits and the biological colonization [3-5].

The obtaining of compatible coatings would be then of the utmost importance, presenting the following advantages: i) Water repellent surfaces would hinder the water uptake minimizing the subsequent decay processes; ii) for coating combining water repellent agents and photocatalysts, also self-cleaning surfaces could be obtained due to the synergistic effect between the photocatalytic oxidation (PCO) of the dirt compounds and the hydrophobicity of the surface that would difficult the anchorage of the stains and would facilitate the removal of the PCO by-products; and iii) finally, biological colonization would be reduced or even avoided by breaking the bonds between microorganisms and substrates by PCO.

While TiO_2 is a recognized photocatalyst that can oxidize dirt components by PCO, it is only efficient under UV illumination [6-8]. In this work nano-heterostructures of of TiO_2/ZnO (50:50 and 10:90) were obtained by Flame Spray Pyrolysis as new photocatalytic agents sensitive towards the visible light spectrum. New coatings were thus designed combining stable dispersions of these nanoparticles with a water repellent admixture (superhydrophobic agent). The coatings were also prepared by adding dispersing agents, superplasticizers, which can avoid the agglomeration of the photocatalytic nanoparticles that is supposed to increase their activity [9]. These new dispersions used as coatings were applied onto sandstone and lime mortar. The study of modified stones and mortars with waterproofing, biocidal and self-cleaning features would be of interest for possible application in preventive conservation of historic buildings. Waterproofing measurements and self-cleaning tests were performed, and photocatalytic activity was also measured through NO_x abatement studies.

Experimental section

Materials

Two different heterostructures of TiO_2-ZnO (50:50 and 10:90) were studied as powder compounds and used to prepare different synergistic superhydrophobic (SPHB) and photocatalytic dispersions further applied as active coatings onto lime mortar and sandstone, as representative building materials of the Cultural Heritage. Nanoparticles of TiO_2-ZnO were synthesized by Lurederra Technological Center by FSP. Previously to their incorporation, nanoparticles were calcined in order to remove all possible nitrogen compounds residual from the synthesis of the nanoparticles.

Calcitic air lime mortars were prepared by mixing 18.3% calcitic air lime supplied by Cal Industrial S.A. (Calinsa Navarra), classified as CL-90 by European regulations and 81.7% standardized siliceous sand (supplied by IETCC) later shaped into cylindrical samples of 3 cm diameter and finally cut around 1 cm high. Rectangular prisms of 5x5x3 cm were obtained for siliceous stone.

Two of the applied coatings were used both in air lime mortar and siliceous stone as dispersions 1% w/v of photocatalyst 50:50 and 1 % w/v photocatalyst 50:50 with a superhydrophobic agent, respectively. While the first dispersion only contains the photocatalyst (pH=5), the second one with superhydrophobic agent (as prepared by Lurederra) consists in an alcoholic solution including photocatalyst. The later was used as a primary dispersion for preparing modified dispersions. The first one was used as control with the aim of proving the PCO efficiency of the new photocatalysts.

Methods

Photocatalyst characterization

Particle size (BET, Table 1), mineralogical composition (XRD, Figure 1) and morphology (TEM, Figure 2) of the two heterostructures were characterized and results are shown below. Heterostructures showed a nanometric size and a mineralogical composition according to the structure between the two main components (TiO_2 and ZnO).

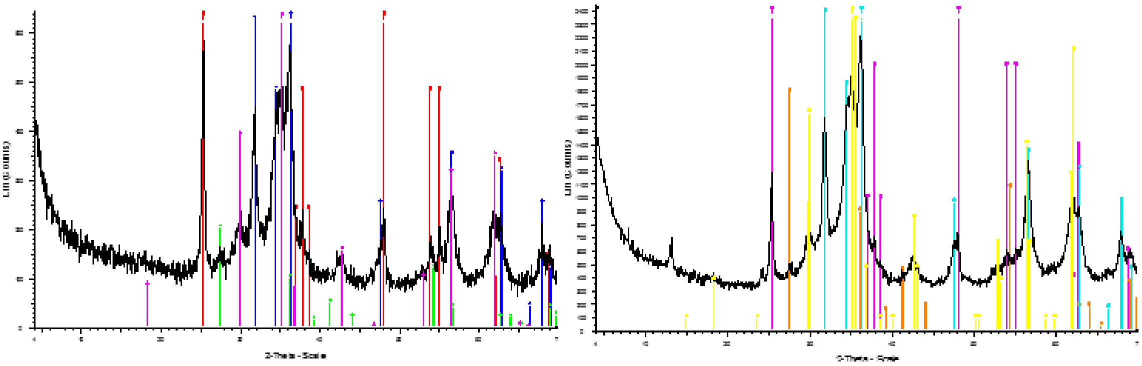

Figure 1. X-ray diffraction patterns conresponding to TiO_2/ZnO 50:50 and TiO_2/ZnO 10:90 samples.

Table 1. BET specific surface area and size of the nano-heterostructures.

Sample	BET (m^2/g)	Estimated size (nm)
TiO_2/ZnO (50:50)	84.8	15
TiO_2/ZnO (10:90)	79.7	19

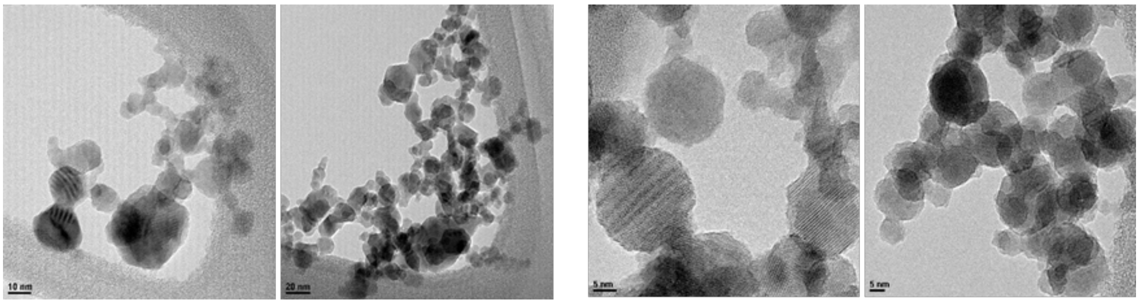

Figure 2. TEM micrographs (Left: TiO2/ZnO 50:50; rigth: TiO_2/ZnO 10:90), showing a mixed morphology between the spherical one of TiO_2 and the elliptical one of ZnO.

Preparation and characterization of superhydrophobic and photocatalytic dispersions

Alcoholic superhydrophobic solutions containing photocatalytic nanoparticles TiO_2/ZnO 50:50 and TiO_2/ZnO 10:90 (1 weight % with respect to the total volume of solution) were the basic media for the preparation of several dispersions using superplasticizers. Active dispersing agents polynaphtalenesulfonate (PNS), polycarboxylate ether (PCE), melamine sulfonate (MEL) and polyacrylate (PA) were added in 1% with respect to the photocatalyst. Table 2 collects a summary of the composition of the dispersions.

Table 2. Composition of the active coatings

COATING NAME	COMPOSITION
P	Photocatalyst 50:50 TiO_2/ZnO in a 1% (w/v) dispersion
SPHB	SPHB dispersion + 50:50 TiO_2/ZnO 1%
PCE-50	SPHB dispersion + 50:50 TiO_2/ZnO 1% + PCE
PNS-50	SPHB dispersion + 50:50 TiO_2/ZnO 1% + PNS
PA-50	SPHB dispersion + 50:50 TiO_2/ZnO 1% + PA
MEL-50	SPHB dispersion + 50:50 TiO_2/ZnO 1% + M
PCE-10	SPHB dispersion + 10:90 TiO_2/ZnO 1% + PCE
PNS-10	SPHB dispersion + 10:90 TiO_2/ZnO 1% + PNS
PA-10	SPHB dispersion + 10:90 TiO_2/ZnO 1% + PA
MEL-10	SPHB dispersion + 10:90 TiO_2/ZnO 1% + M

Particle size distribution measurements of these dispersions were carried out by means of Malvern Mastersizer laser diffractometer equipment.

Application of the dispersions on different building materials

The as-prepared dispersions were applied onto siliceous stone samples and air lime mortars by simple deposition using a pipette, pouring 1 mL in order to cover the whole surface and leaving the sample drying for 24 hours under lab conditions.

Photocatalytic studies: NOx oxidation

The photocatalytic activity of the nanoparticles was studied in a laminar-flow reactor (ISO 22197-1 [10]), under UV, solar and visible radiation, using a cut-off filter for the last one. The initial concentration of NO was fixed to 500 ppb and concentrations of NO and NO_2 were determined by using a chemiluminescence detector (Environnement AC32M) at a 3.0 L·min−1 flow.

The photocatalytic effect of the coatings applied onto air lime mortars and sandstone was also studied under UV and solar conditions following the same experimental conditions. Active nanoparticle powders were tested for 5 hours. Since the initial trials proved that the values of NO_x abatement were constant, the test time was then reduced to 30 min for the coatings.

Samples were subjected to an accelerated ageing process in a climatic chamber, according to the steps depicted in Table 3. After that, photocatalytic activity of the samples was again measured to establish the durability of the active coatings.

Table 3. Characteristics of the cycle of accelerated weathering

Cycle duration	Step	Temperature (°C)	Relative Humidity (%)	Rain	UV Light	Time (min)
24 h	1	35	30	No	Yes	160
	2	12	80	Yes	No	160
	3	20	50	No	No	160
	4	12	60	No	No	160
	5	35	30	No	Yes	160
	6	12	80	Yes	No	160
	7	35	30	No	Yes	160
	8	20	50	No	No	160
	9	12	60	No	No	160

Hydrophobicity studies

Using a video-based optical contact angle measuring instrument (OCA 15EC Dataphysics), the static water contact angle (WCA) of the treated surface of the samples was registered. Droplets of 5 µL deionized water were poured and monitored during 10 s, in order to achieve reliable data [9, 11].

Self-cleaning test

First, 1 mL of a 10^{-3}M Rhodamine B solution was poured on top of three different samples of sandstone and lime mortar: non-treated sample (Control), dispersion of 1 % photocatalyst TiO_2/ZnO 50:50 heterostructure (Photocatalyst), dispersion of both 1% TiO_2/ZnO 50:50 photocatalyst and superhydrophobic agent (SPHB). One minute after the application the samples were moved vertically and left for 1 hour, and photos were taken.

In the second part of the test 1 mL of the previously prepared Rhodamine B solution was poured on the six samples that remained in horizontal position. Meanwhile, a UV lamp was placed about 30 cm on top of the sample. The light was set on and photos were taken at times 0, 10, 15, 30, 45, 60, 75, 90, 120, 300, 480 min and 24 h.

Results and discussion

Characterization of PSD of superhydrophobic-photocatalytic dispersions

Figure 3 shows the particle size distribution (PSD) of dispersions with nano-heterostructures TiO_2/ZnO 50:50. Control 1 corresponds to dispersion with just the photocatalyst, showing a unimodal PSD, with a maximum at 18 µm. When this dispersion was modified upon the addition of SPHB agent, nanoparticles tended to agglomerate, yielding a maximum at around 60 µm (Control 2).

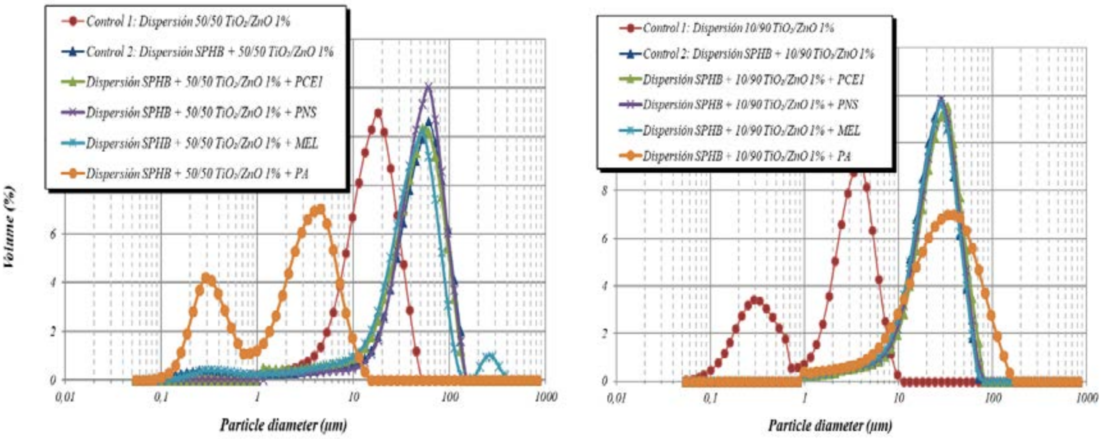

Figure 3. Particle size of the superhydrophobic-photocatalytic dispersions.

Superplasticizers were also added with the aim of preventing nanoparticles from agglomeration. PNS did not show any efficiency in reducing the size of the agglomerates, whereas very slight improvements could be detected for PCE1 and MEL polymeric superplasticizers. Maybe the dosage of these SPs should be modified to reach an effective dispersion of nanoparticles.

The only exception was the dispersion with PA, which showed a bimodal PSD with maximum values at 0.3 µm and 3.9 µm.

As for the PSD of nano-heterostructures TiO_2/ZnO 10:90 (Figure 3, right), the dispersion of just photocatalyst depicted lower size of agglomerates than that of the TiO_2/ZnO 50:50 and a bimodal distribution with two maximums at 0.3 and 4 µm. The presence of the SPHB agent caused the agglomeration of the nanoparticles, although a smaller particle diameter, of around 30 µm, was obtained compared with the TiO_2/ZnO 50:50 dispersion.

PCE 1, PNS and MEL superplasticizers hardly modified the PSD, whereas PA did not perform as well as in the case of the TiO_2/ZnO 50:50 dispersions.

Photocatalytic performance

Photocatalytic activity of ZnO and TiO2 powder nano-heterostructures

The photocatalytic activity of the original nanoparticles in powder was studied and compared with pure TiO_2 and pure ZnO nanoparticles (Figure 4 and Figure 5). With respect to pure ZnO, the newly synthesized heterostructures improved their activity and increased both the NO and NO_x abatements. As compared with pure TiO_2, the NO abatement of the two heterostructures was slightly lower although NO_x removal was higher. This was ascribed to the higher NO_2 release provoked by the TiO_2 action.

As main conclusion, the nano-heterostructures evidenced outstanding photocatalytic activity, yielding better NO_x removal rates than those of pure semiconductor oxides like ZnO or TiO_2. TiO_2/ZnO 10:90 seems to be a little more efficient than TiO_2/ZnO 50:50.

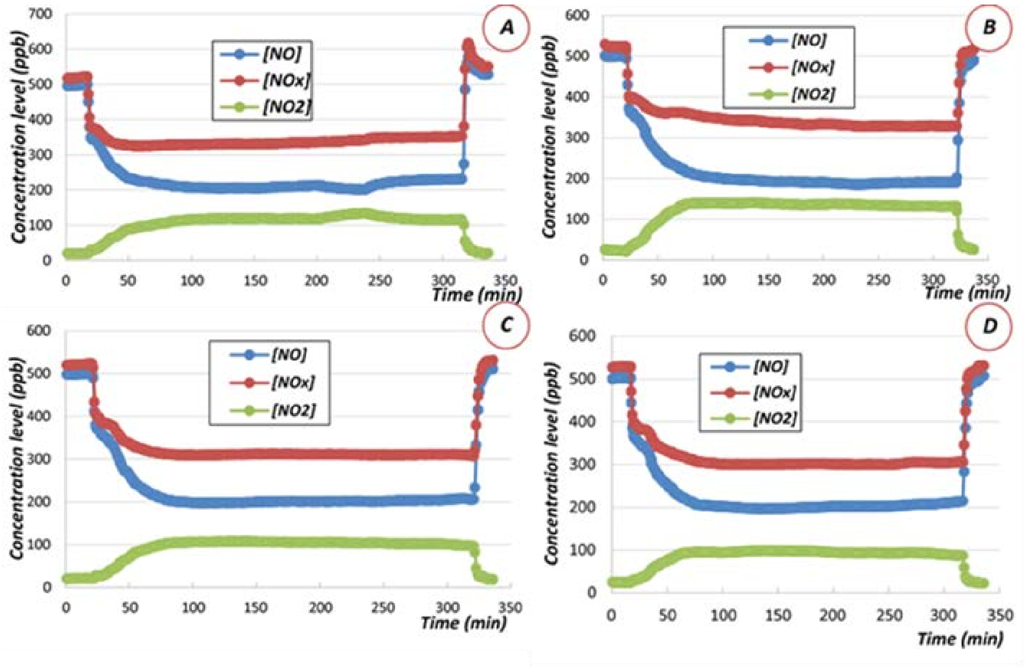

Figure 4. Profiles of NO, NO2 and NOx abatements for ZnO (a), TiO_2 (b) and the heterostructures TiO_2/ZnO 50:50 (c) and 10:90 (d).

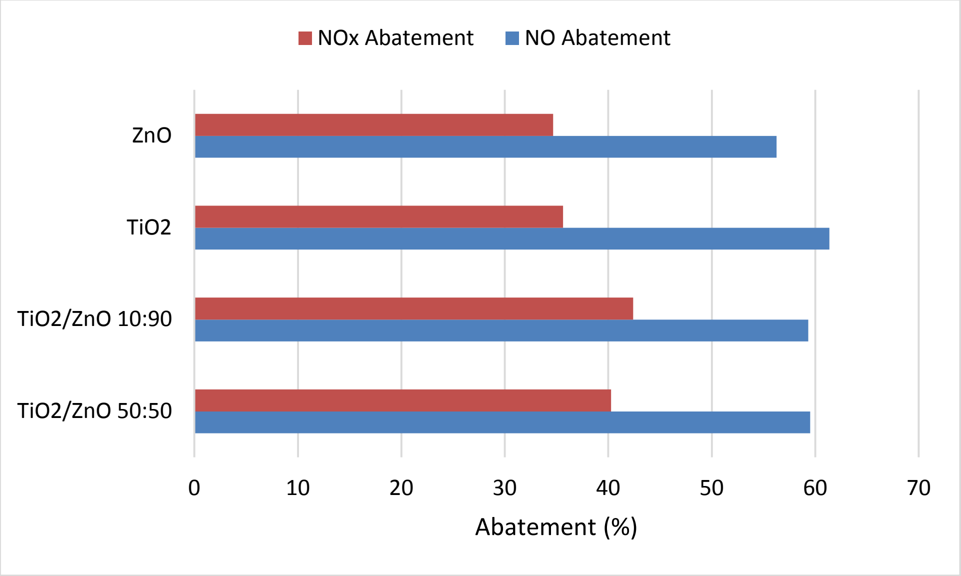

Figure 5. NO abatement values of TiO_2, ZnO and the two heterostructures.

Photocatalytic activity of the coatings with nano-heterostructure TiO2/ZnO 50:50.

After applying the active coatings onto sandstone, results showed that the presence of the photocatalyst increased the activity under both UV and solar radiation (Figure 6) as compared with the non-treated specimens. When the coatings were prepared with SPHB agent, the photocatalytic activity underwent a decrease, suggesting a certain degree of undesirable interaction. This finding could be ascribed to the blockage of active sites of the photocatalyst or to the absence of the necessary water for the PCO due to the hydrophobic environment caused by the SPHB admixture.

For the coating including SFHB and photocatalyst, the sandstone treated samples showed the highest efficiency in NO removal under UV illumination, whereas under solar light illumination were the lime mortar samples. The observed decrease in NO removal from UV to solar light illumination is ascribed to the different quantum efficiency between the UV and solar photons.

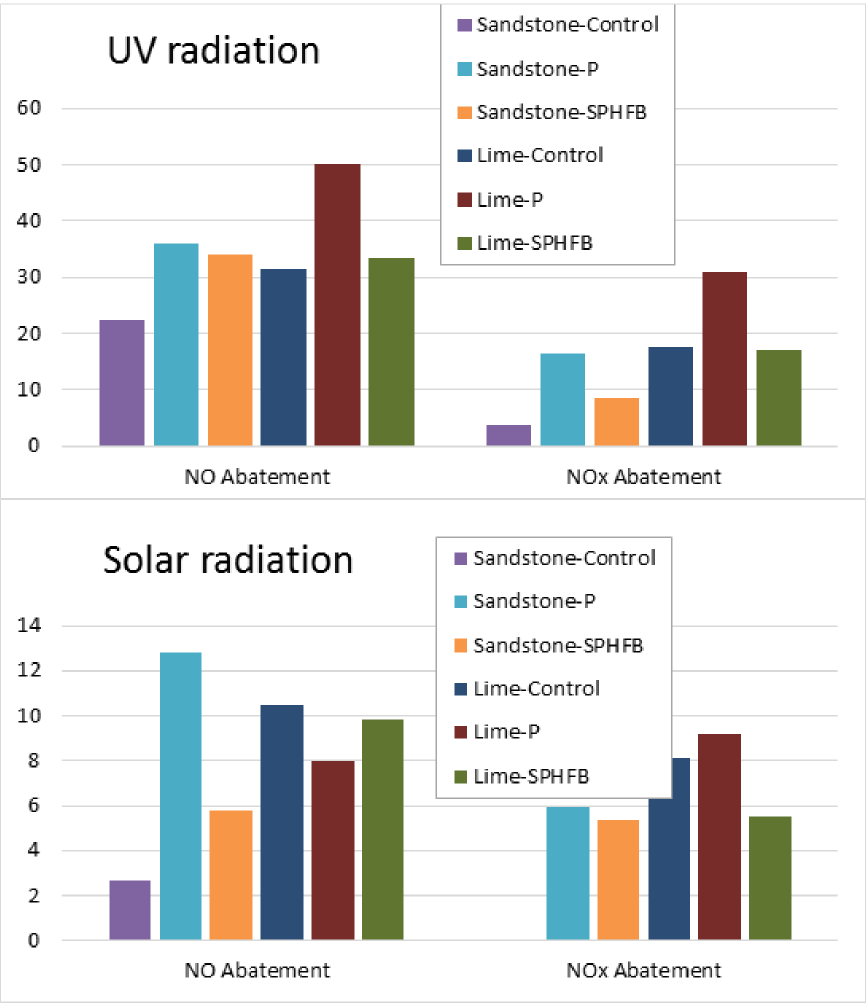

Figure 6. NO and NOx abatement of different samples treated with active coatings: non-treated sample (Control), only heterostructured photocatalyst TiO_2/ZnO 50:50 in a 1% (w/v) dispersion (P); and a dispersion containing both photocatalyst and superhydrophobic agent (SPHB).

Generally speaking, the higher activity of the lime samples (control and treated samples as well) can be explained owing to the occurrence of secondary reactions (mainly NO disproportionation) due to the highly alkaline medium of the mortar.

Effect of the superplasticizers: photocatalytic activity of the coatings with nano-heterostructures TiO_2/ZnO 10:90 and 50:50 including dispersing agents

A comparison between the samples treated with coatings modified with SPs was carried out to ascertain the influence of the dispersing agents on the photocatalytic performance of the coatings. Figure 7 collects the results, being the control a sample of raw material with no coating applied.

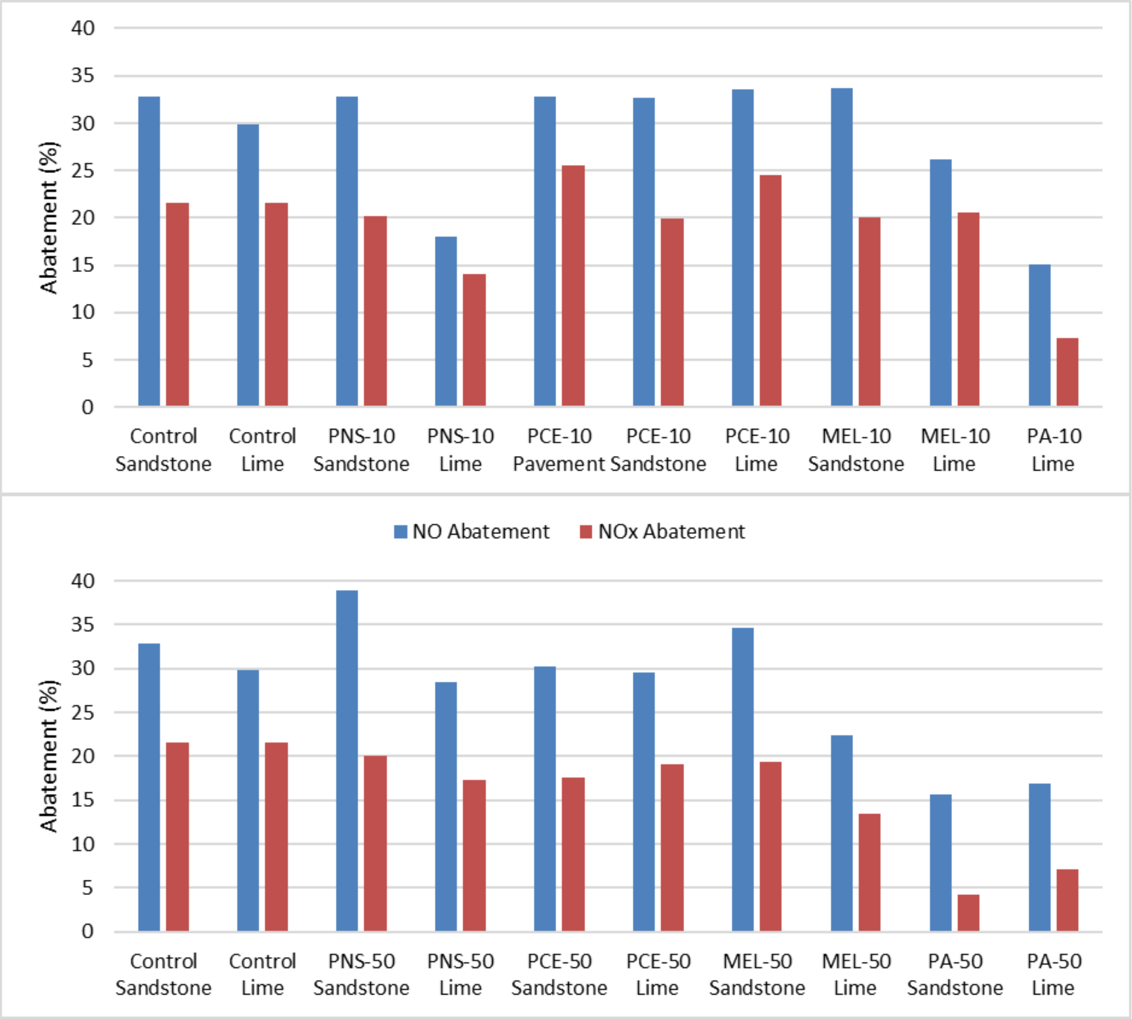

Figure 7. Effect of the different dispersing agents: NO and NOx abatement of the coatings prepared with TiO_2/ZnO 10:90 (top) and 50:50 (bottom) photocatalysts.

The majority of the samples showed NO_x abatementes higher than 25%. On one hand, trated sandstone samples showed similar results and all of them improved the NO and NOx abatements with respect to the control. The results of lime samples were not uniform and only the treatment with PCE-10 showed a higer NO_x abatement than that of the control. It should be noted that MEL and PNS aditives works well with coating applied to the siliceous stone but not with the coatings applied to lime mortar. It has to bear in mind that the active surface of the stone (15 cm^2) is more than twice of that of the mortar (7 cm^2).

The most interesting samples in terms of PCO efficiency were subjected to accelerated weathering in a climatic chamber following the cycles described in the Experimental section. Then, the results of NO_x abatement were again recorded and showed in Figure 8. It can be observed that climatic ageing caused a decrease in the photocatalytic activity, but samples still yielded NO_x abatements higher than 20%, involving a reasonable durability of the active coatings.

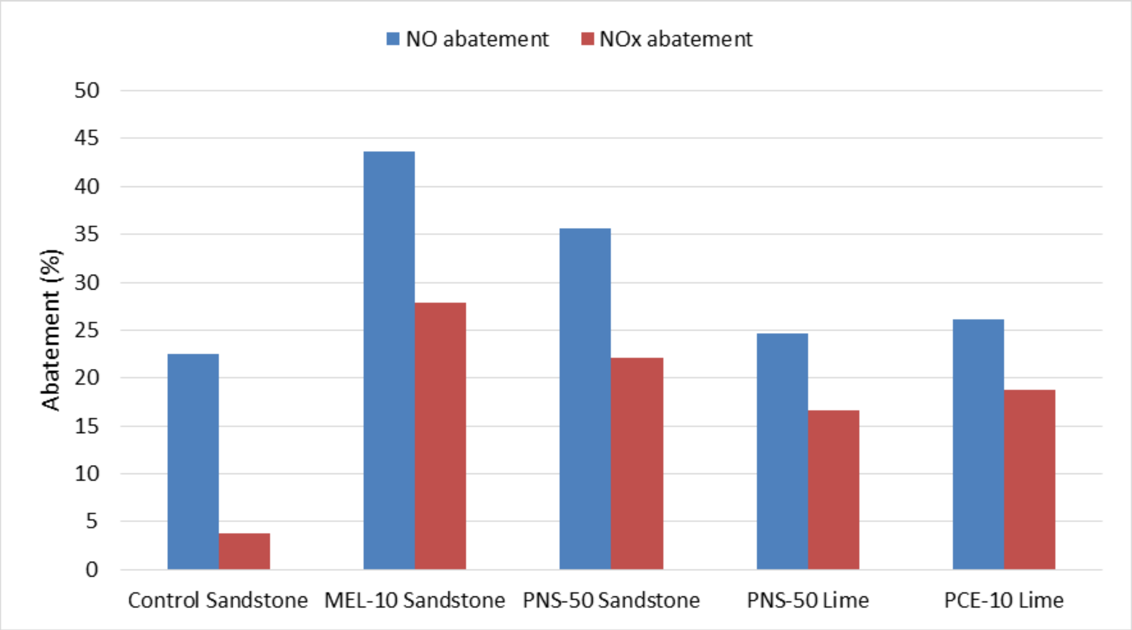

Figure 8. NO and NO_x abatement of the samples with better results after accelerate weathering treatment.

Waterproofing studies

The majority of the treated samples were seen to have WCA higher than 100°, suggesting a high efficiency of the SPHB agent and a good compatibility with the photocatalytic additives (Table 4).

Table 4. Water contact angle of the samples treated with TiO_2/ZnO 10:90 photocatalyst.

Sample	ϴ	Partial Absorption of the drop of water
Lime-Control	< 10	Yes
Lime-MEL	82.9	No
Lime-PA	129.6	Yes
Lime-PCE	131.7	No
Lime-PNS	87.3	No
Sandstone-Control	11.5	Yes
Sandstone-MEL	142.6	No
Sandstone-PA	119.5	Yes
Sandstone-PCE	131.7	No
Sandstone-PNS	131.7	No

The presence of the SPs was not detrimental for the hydrophobization of the surfaces of the treated stones and mortars, with the exception of the coatings bearing melamine sulfonate and polynaphtalene sulfonate applied onto air lime mortars. This result might be explained as a consequence of the dosage and compatibility of the SP with the strong alkaline lime medium. Also, it should be noticed that both substrates treated with PA-bearing coating showed a tendency to absorb the water drop over the time. Maybe the PA creates strong hydrogen bonds with the water drop, jeopardizing the hydrophobic protection of the coatings.

Self-cleaning tests

SP-free coatings were applied onto sandstone and lime mortars to assess the self-cleaning ability of the photocatalyst and of the SPHB-photocatalyst coatings. In this test, the objective was to identify if the coating was able to efficiently degrade the organic dye deposited on the surface of the sample, as represented below (Figure 9 and Figure 10). Samples were observed along the time. Results gathered at different times are represented in Table 5, being the levels of degradation at naked eye: 0 no degradation, 1 slight degradation, 2 sharp degradation and 3 total degradation.

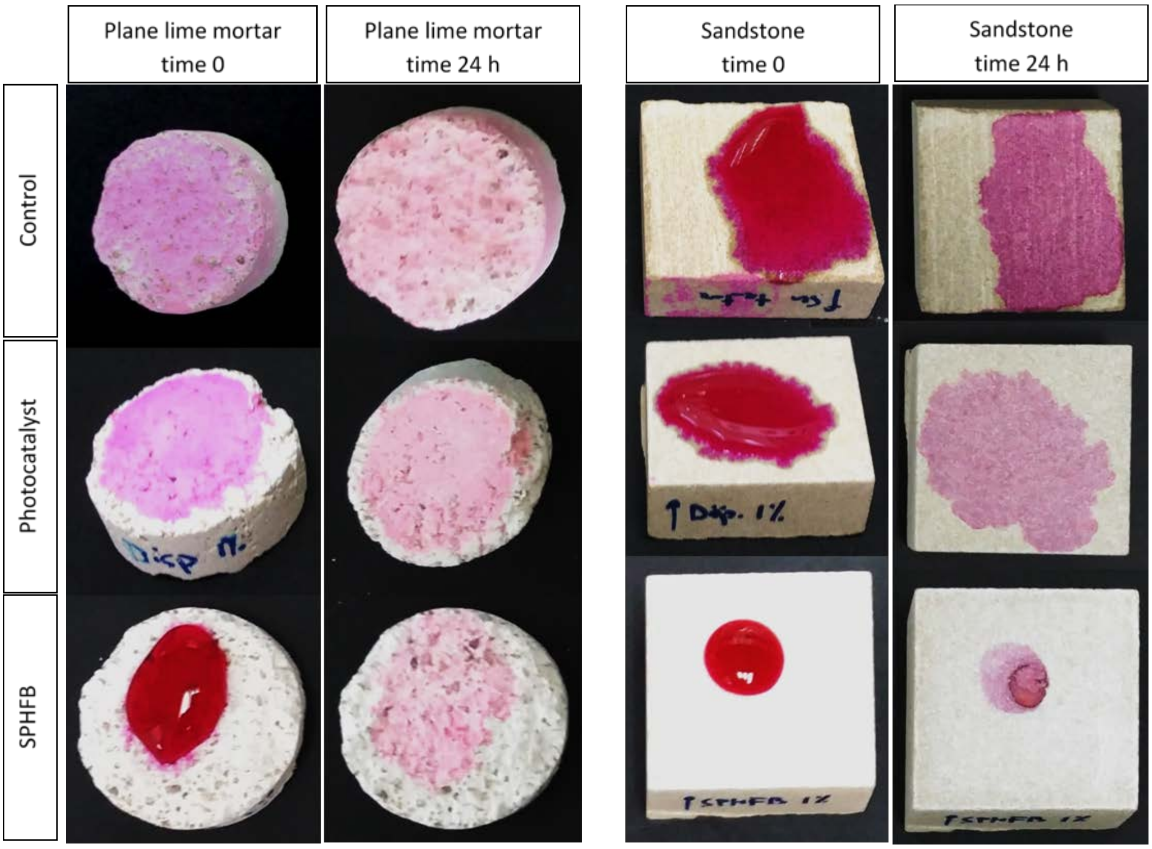

Figure 9. Results of the photocatalytic self-cleaning test at time 0 and 24h for lime mortar and siliceous stone samples. White coloring in Sandstone at time 0 is due to the light source.

Results showed that the non-treated specimens were fully affected by the dye deposition, with a large degree of dye penetration from the surface to the inner part of the substrate. After 24 hours, the stain provoked by the dye was evident, showing, if any, negligible degradation of the dye (0 value in Table 5).

Table 5. Degradation levels for the photocatalytic self-cleaning test.

Degradation level	**Time (min)**	**0**	**10**	**15**	**30**	**45**	**60**	**75**	**90**	**120**	**300**	**480**	**1440**
	Lime-Control	0	0	0	0	0	0	0	0	0	0	0	0
	Lime-Photocatalyst	0	0	0	0	1	1	1	1	1	1	1	2
	Lime-SPHB	0	0	0	0	0	0	1	1	1	1	2	2
	Stone-Control	0	0	0	0	0	0	0	0	0	0	0	0
	Stone-Photocatalyst	0	0	0	0	0	1	1	1	1	1	1	2
	Stone-SPHB	0	0	0	0	0	0	0	0	1	1	2	2

The coating applied with photocatalyst was much more efficient in reducing the intensity of the colour of the dye's stain. This is a clear evidence of the positive action of the photocatalytic additive. Finally, the coating including both photocatalyst and SPHB agent showed a synergistic and positive effect on the dye degradation: on one hand, the superhydrophobicity hindered the adsorption and penetration of the dye, as can be observed in the photographs at time 0; and, on the other hand, photocatalyst was able to oxidize the pigment along the time.

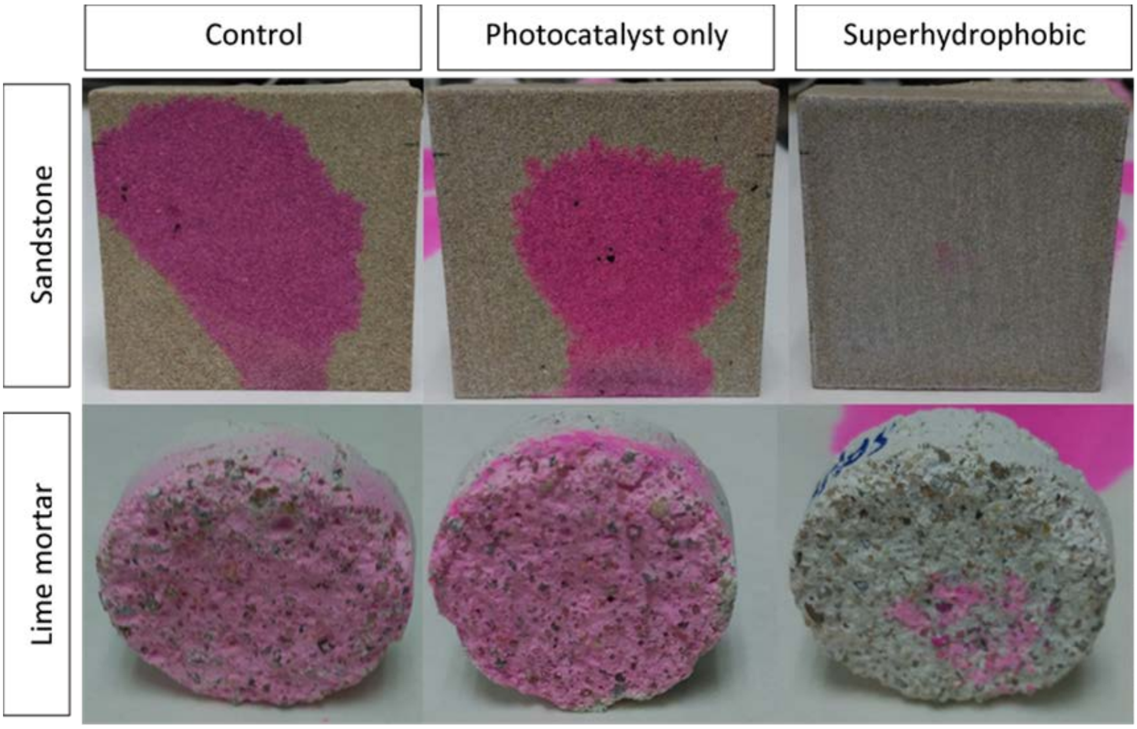

Figure 10. Results of the self-cleaning test for samples in vertical position: dye was deposited onto lime mortar and siliceous stone samples for one minute in horizontal position and then moved to vertical position.

The self-cleaning ability was also measured for these materials placed in vertical position. As expected, the superhydrophobic effect is extremely important for preventing the dye from being absorbed and thus retained. As shown in Figure 10, the dye is practically not retained for samples with SPHB agent.

Conclusions

New coatings with self-cleaning and superhydrophobic abilities have been prepared and applied onto air lime mortar and siliceous stone. The objective of these coatings was to obtain modified stones and mortars with waterproofing, biocidal and self-cleaning features that would be of interest for application in preventive conservation of historic buildings. The coatings have been obtained combining stable dispersions of nano-heterostructures of TiO_2/ZnO (50:50 and 10:90) and a water repellent admixture (superhydrophobic agent). These new photocatalytic agents were seen to be sensitive towards the visible light spectrum.

In addition, dispersing agents, superplasticizers, were also in some cases added with the purpose of avoiding the agglomeration of the photocatalytic nanoparticles to increase their activity.

Photocatalytic activity of the treated specimens was seen to increase due to the active coatings. Combination of photocatalyst with SPHB agent slightly reduced the activity of the former. NO abatement measurements were favoured in the case of air lime mortars most probably ascribed to the highly alkaline pH.

Self-cleaning tests showed a positive synergistic effect between photocatalyst and SPHB agent, reducing the dye adsorption and absorption and degrading the organic pigment by photocatalytic oxidation.

Concerning the use of SPs, most interesting results were obtained for the dispersions of melamine sulphonate with TiO_2/ZnO 10:90 on sandstone and polycarboxylate ether applied onto lime mortar, in both superhydrophobic and photocatalytic activities.

Despite having good particle size, dispersions with PA did not provide good results of NO_x abatement and this finding has been correlated with the concentration of the polymeric additive.

The future perspectives require water vapor permeability measurements to be carried out later on in order to understand the real behavior of the coating once applied to Architectural Heritage materials. Optimization of some dosages of the admixtures should be also envisaged.

Acknowledgments

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