

Titania and Silica Nanoparticle-Modified Coatings for Cementitious Materials

Qingxu Jin, Marisol Faraldos, Ana Bahamonde, Behnaz H. Zaribaf, Kimberly E. Kurtis

Synopsis: Due to the ubiquity of concrete in the urban environment and the upscaling of nanomaterial production, the incorporation of nanoparticles into cementitious materials has gained increased attention. This study compares the performance of various titania (TiO_2) and silica (SiO_2) nanoparticles-modified coatings, including their photocatalytic performance and the quality of their adhesion to the cementitious substrates. The photocatalytic performance with respect to air purification and self-cleaning are evaluated by nitrogen oxide (NO_x) and methylene blue (MB) dye photodegradation, respectively. The results show that the Portland cement (OPC)-based cementitious materials exhibit greater photocatalytic efficiency than calcium aluminate cement (CAC)-based ones. It is proposed that the superior performance is due to a greater proportion of finer porosity and the presence of high surface area calcium silicate hydrates (C-S-H) in OPC-based cementitious materials. Interactions between coatings and cementitious substrates are examined through wettability and adhesion. The results show that the inclusion of silica layer can affect the interaction of coated cementitious surface with water, as well as the bond strength between coating and cementitious substrate.

Keywords: Self-cleaning; Air purification; TiO_2 ; SiO_2 ; NO_x ; Coating; Photocatalytic cementitious materials

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INTRODUCTION

Due to the ubiquity of concrete in the urban environment and the upscaling of nanomaterial production, the incorporation of photocatalytic titanium dioxide (TiO_2) nanoparticles into cementitious materials has gained increasing attention in the construction and building industry. It has been demonstrated that TiO_2 -containing cementitious materials can be applied to building façades, exterior tiles, roofs, and concrete pavements for improved performance^{1,2,3}. Two of their major contributions through photocatalytic reactions are air purification^{4,5} and self-cleaning^{6,7}. For air purification, they can effectively remove smog-producing nitrogen oxides (NO_x) from the atmosphere in the presence of water, oxygen, and UV or near UV-light^{8,9}. Considering the difficulty of mitigating urban NO_x levels due to lack of air flow, intense road traffic, and proximity to industrial zones, the use of TiO_2 -containing cementitious materials in concrete infrastructure and building surfaces could be an effective means to improve air quality. In addition, photo-degradation of organic pollutants could also occur on the surfaces of the TiO_2 -containing cementitious materials, adding valuable “self-cleaning” properties, which maintain the aesthetic characteristics of concrete urban environment and minimize the cleaning expenses^{10,11}. Because the photocatalytic reactions are surface phenomenon^{12,13}, it would be more effective and economically efficient to apply TiO_2 -modified coatings to the surface of cementitious material.

In order to increase the durability and reduce the cost of the TiO_2 -modified coatings, researchers have proposed to include silica (SiO_2) in the TiO_2 -modified coatings since the production of SiO_2 is less expensive than TiO_2 and SiO_2 has higher mechanical and thermal stability than TiO_2 ^{14,15,16,17}. In addition to low cost and high durability, the introduction of SiO_2 also alter the hydrophilicity of coated surfaces¹⁸. A hydrophobic coated surface can be achieved through the application of hydrophobic SiO_2 . This could help address the durability problems of cementitious substrates due to the penetration of water and aggressive chemicals when exposed to atmosphere conditions of relative humidity greater than 50%^{19,20}. However, concerns about bond strength between the TiO_2 - SiO_2 coating and cementitious substrates have been raised²¹, and thus the bonding of coated surface is also of interest.

While the photocatalytic performances of TiO_2 - SiO_2 coated cementitious materials depend on the durability and composition of the coating, recent studies have shown that the microstructure of cementitious materials also plays an important role in the photocatalytic performance^{22,23}. To understand the correlation between the microstructure of different cementitious materials and their photocatalytic performances, two types of cement will be selected as substrates in this paper: ordinary Portland cement (OPC) and calcium aluminate cement (CAC), whose different chemical composition and hydration lead to different microstructures. The details of different TiO_2 and SiO_2 - modified coatings will be described and their photocatalytic performances (i.e. air-purification and self-cleaning) are evaluated by NO_x degradation and Methylene Blue (MB) methods, respectively. The interactions between the different coatings and these cementitious substrates will also be investigated. Finally, a recommendation for selecting coating design will be provided.

EXPERIMENTAL

Preparation and characterization of cementitious substrates

The cementitious substrates were prepared from two types of cements: ASTM C150 Type I/II Portland cement (OPC) and calcium aluminate cement (CAC). The water-to-cement ratio for all mixtures was at 0.40. The chemical compositions of the cements are provided in Table 1.

To produce cementitious substrates, deionized water (18.2 m Ω -cm (7.2 m Ω -inch)) was added to the cement and mixed for two minutes using a handheld electric mixer. Plate samples, 50 × 50 × 10 mm (2 × 2 × 3/8 inch, width × length × height), were cast against a smooth surface without any use of a release agent and stored at room temperature around 23 °C (74 °F) for the first 24 hours under plastic sheeting covered container with 100% relative humidity. The plate samples were removed from their molds after 24 hours and subsequently cured in limewater at room temperature of 23 °C (74 °F) for 28 days. After curing, the cement paste surfaces were polished using 600-grit sandpaper. Prior to the application of photocatalytic coatings, all samples were conditioned at room temperature and 50 % relative humidity until there was no significant mass change (change of less than 0.5% over a 6-hour period). According to X-ray diffraction (XRD) analysis, the conversion of the CAC samples was low. This was expected due to the relatively low curing temperature and low age at the time of testing²⁴.

TABLE 1 - CHEMICAL COMPOSITIONS OF OPC AND CAC CEMENTS.

Cements	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	LOI
OPC	19.2	4.5	3	62.8	3.6	3.1	0.5	2.6
CAC	5.5	45.2	6.9	37.7	0.2	0.07	0.26	1.9

Preparation and characterization of photocatalytic coatings

Different synthesis methods have been proposed to produce TiO_2 - SiO_2 composite coatings in past decades, including direct methods^{25,26}, precipitation method²⁷, and the sol-gel methods²⁸. In this paper, a direct method was used of applying TiO_2 and SiO_2 sol-gel layers on the cementitious substrate. For samples that contain both TiO_2 and SiO_2 layers, the SiO_2 layer was first applied on the surface by uniformly spraying SiO_2 sol-gel suspensions on the cementitious substrate and then dried at room temperature of 23 °C (74 °F) overnight; then the TiO_2 layer was applied on the top of the coated surface to produce the final composite coatings. The thickness of the applied layers was estimated by dividing volume of suspension applied on the surface of cementitious substrate by the surface area of the substrate. Since the area of the substrate was the same for each sample and the coating was uniformly applied, the coating thickness was kept the same in this study. Previous study has also demonstrated that as long as the coating is uniformly applied on the surface of the substrate and covers the entire surface, the photocatalytic capability is the same regardless of the coating thickness²¹.

Three sol-gel suspensions were used to make coatings: 1) a lab-produced TiO_2 suspension, which was prepared by adding 8.25 mL (0.278 oz) of titanium isopropoxide hydrolysis (97%) in acid media, which was obtained by adding 0.71 mL (0.024 oz) of HNO_3 (65%) to 100 mL (3.380 oz) of deionized (DI) water. The concentration of the lab-produced TiO_2 suspension is 22±2 g of TiO_2 per liter of suspension (g/L); 2) a commercial hydrophobic SiO_2 sol-gel suspension based on siloxanes and its concentration is 5±1 g/L; and 3) a lab-produced hydrophilic SiO_2 suspension, which was prepared by adding 15 mL (0.507 oz) of tetraethylorthosilicate hydrolysis (>98%) in the same acid media as the one in 1). The concentration of the lab-produced hydrophilic SiO_2 suspension is 26±3 g/L. The pH of both

lab-produced TiO_2 and SiO_2 suspensions was 2.5-3.0. The TiO_2 suspension was prepared by the anatase phase, confirmed by X-ray diffraction (XRD) analysis, as it is considered more photocatalytically active than rutile phase²⁹. According to XRD analysis, both silica suspensions were amorphous. Different cementitious substrates and coating schemes were used to compare the photocatalytic and adhesive performance, and their nomenclatures summarized in Table 2.

The characterizations of photocatalytic coatings are as follows: the porosity of cementitious samples was studied by mercury intrusion porosimetry (MIP) method, assuming a cylindrical non-intersecting pore model, with the values recommended by the IUPAC of 141° and 484 mN/m (0.09 lb/in), for the contact angle and surface tension of mercury, respectively. A cubic sample was carefully cut from the plate substrate with the length of 0.8 cm to ensure the piece could be introduced into the sample holder for MIP analysis. When placing the sample into the sample holder, the coated surface is always facing up. The hydrophilicity and hydrophobicity for all photocatalytic-cements were determined by measuring the contact angle of the water drop over the solid surface using the software www.geogebra.org. The image of the water drop on the sample surface was acquired by USB microscope. Adhesion tests were performed following ASTM D3359³⁰, using a standardized multi-cutter. The scanning electron microscopy (SEM) images of the coated surface after the adhesion tests were obtained by tablet Microscope.

TABLE 2 – CEMENTITIOUS SUBSTRATE, COATING SCHEME, NOMENCLATURES AND TEST RESULTS OF PHOTOCATALYTIC CEMENTITIOUS MATERIALS.

Sample ID*	OPC	CAC	Coating composition			Test results		
			T	S1	S2	Contact angle (°)	NO _x conversion (%)	50% MB dye bleaching t _{1/2} (min)
PB	×					13	0	-
PT	×		×			0	65	260
PS1	×			×		156	0	-
PST1	×		×	×		103	52	1990
PS2	×				×	0	0	-
PST2	×		×		×	6	60	980
C4B		×				11	0	-
C4T		×	×			6	50	230
C4S1		×		×		130	0	-
C4ST1		×	×	×		131	32	295
C4S2		×			×	8	0	-
C4ST2		×	×		×	6	40	3280

* Sample ID: P – OPC, C4 – CAC, B – blank cementitious materials (control), T- lab-produced TiO_2 , S1- commercial hydrophobic SiO_2 , and S2 – lab-produced hydrophilic SiO_2 . For example, PST1 indicates OPC substrate topped by a titanium dioxide layer followed by a layer of the commercial silica suspension

Nitrogen oxide (NO_x) photo-degradation test

The NO_x photo-degradation tests were performed following procedures in the ISO 22197³¹ and JIS R 1701 Standards³². The test setup is shown in Figure 1. Three identical cement plates with a total area of 75 mm² (0.116 in²) were placed in the reaction chamber under two 40W UV fluorescent lamps with peak emission at 365 nm. The intensity of UV light at the sample surface was maintained at 10 Wm⁻². A mixture of 1 ppm nitric oxide (NO) gas and ultrapure dry air blew through the reaction chamber at a total flow rate of 1 L·min⁻¹ (33.814 oz/ min⁻¹). The chamber was held at a constant temperature of 23 °C (74 °F) and a relative humidity of 50%. The initial gas concentration was kept at ~1000 ppb before turning on the UV light. Once the concentration stabilized, the UV light exposure started and continued for 5 hours. After the UV light was turned off, the concentration was allowed to stabilize. The gas concentration was continuously measured by chemiluminescent NO/NO₂/NO_x analyzer. To investigate the long-term performance of NO_x abatement, PT and C4T were selected for a consecutive two-cycle test. Each cycle had a consecutive 5-hour NO_x and UV light exposure followed by a 12-hour break, using the same testing conditions as single cycle test. Samples were not treated during the breaks.

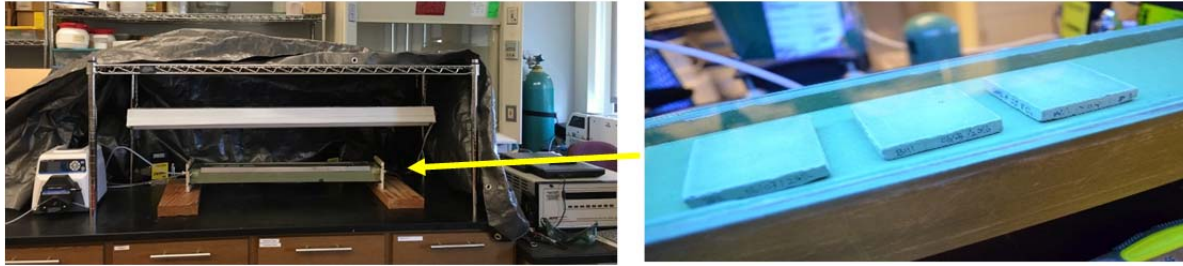


FIGURE 1 – SETUP FOR (NO_x) PHOTO-DEGRADATION TEST.

Methylene blue (MB) dye photo-degradation

MB dye photo-degradation tests were conducted in a closed and refrigerated chamber at a constant temperature of 23 °C (74 °F), equipped with six 15W Black Blue Light fluorescent lamps which emit UV light with wavelengths centered at 365 nm. The samples received irradiance of 20 W·m⁻² based on the previous study²¹. The detailed procedure and determination of the amount of MB required to provide enough color contrast can also be found in that study²¹. The spot of MB dye was applied by depositing 0.1 mL (0.003 oz) of 3.2 x 10⁻³ M methylene blue solution in the solution of water: acetone (50:50 wt%) on the surface of samples. The MB photo-degradation was quantitatively measured by UV-Vis diffuse reflectance spectroscopy at irradiation periods from 0 to 3750 mins.

RESULTS AND DISCUSSION

Characterization studies

Figure 2 shows the pore size distribution of all studied photocatalytic cementitious materials. For OPC samples, the results suggest that coatings did not significantly affect the surface porosity or pore structures. For CAC samples, variations were observed in peaks of 200-300 nm, 2000 nm, and 20000 nm. This suggests that the coatings alter the surface porosity and pore structures of CAC samples. Further studies are needed to understand the fundamental mechanism of the coatings' effect on surface microstructures. It should be emphasized that important differences were observed between OPC and CAC samples. OPC samples show a greater proportion of pores smaller than 100nm, with a maximum macropore size of around 45-100 nm, compared to CAC. CAC samples show a pore size distribution with three well-defined macropores of 100, 2000, and 20000 nm, significantly coarser than those in the OPC. These differences likely relate to the inherent variations in the hydration product morphology of these two cementitious systems and could affect the photocatalytic performances of OPC and CAC based cementitious materials³⁴.

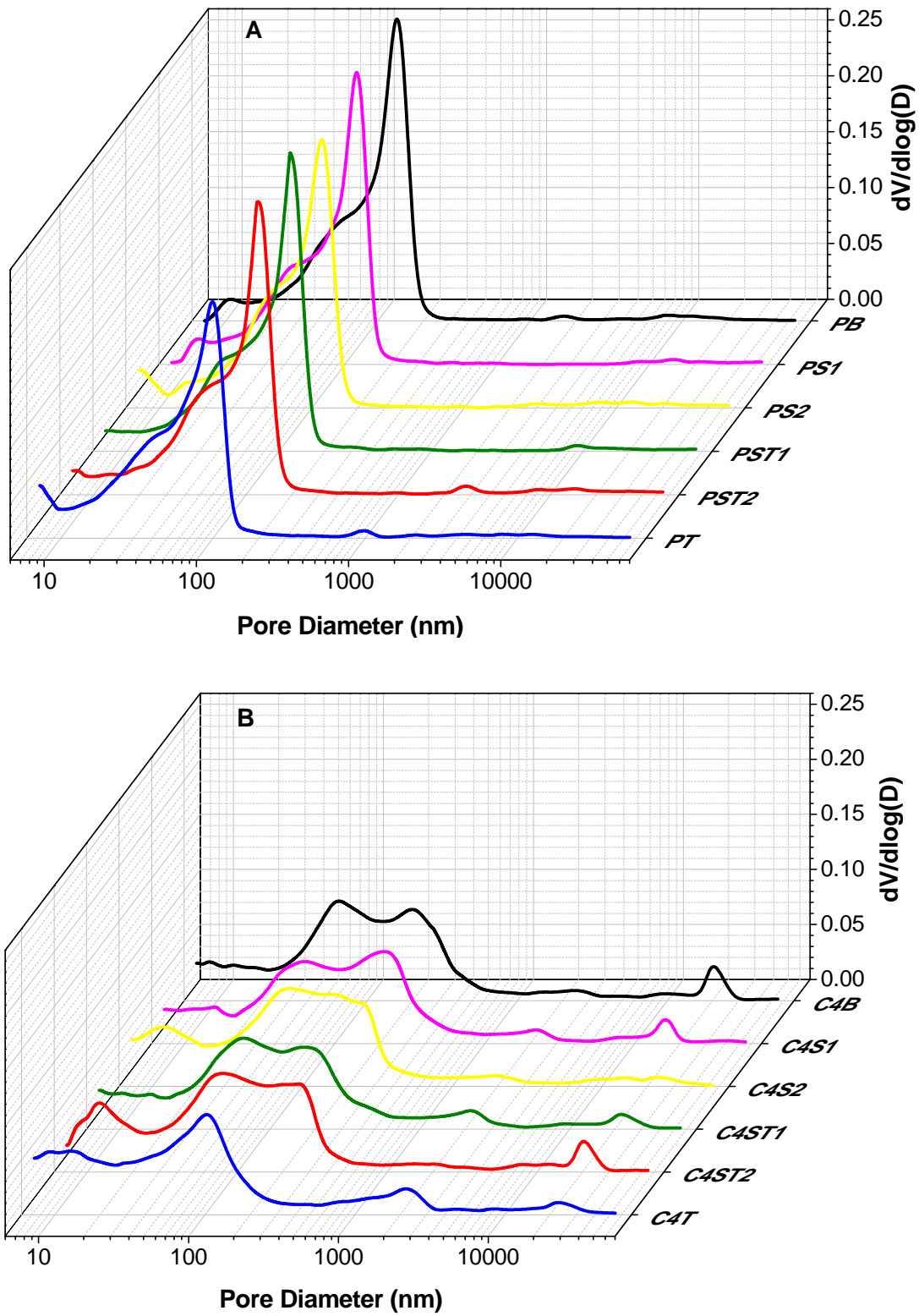


FIGURE 2 - PORE SIZE DISTRIBUTION OF CEMENTITIOUS MATERIALS, WITH EACH OF THE PHOTOCATALYTIC COATINGS: (A) OPC AND (B) CAC

The hydrophilicity and hydrophobicity of the photocatalytic cementitious material surfaces were studied by the wettability test. The results show the interactions between the sample surfaces and water. The contact angles of all coated samples are provided in Table 2. Based on the previous studies^{35,36,37}, surfaces of photocatalytic cementitious materials with contact angles smaller than 90° are considered hydrophilic and with contact angles larger than 90° are considered hydrophobic. The uncoated control samples (PB and C4B) were found to have contact angles of 13° and 11°, respectively. This indicates that the surfaces of cementitious substrates are hydrophilic, which is expected. Thus, by applying different coatings to the surfaces of cementitious materials, hydrophilicity could be altered. Samples with only lab-produced TiO₂ coating (PT and C4T) exhibited hydrophilic surfaces. This indicates the TiO₂ coating should also be hydrophilic. Samples with lab-produced SiO₂, with or without the second TiO₂ layer (PS2, PST2, C4S2, and C4ST2), also exhibited hydrophilic surfaces. This is also expected as the lab-produced SiO₂ is made to be hydrophilic. In contrast, the samples with commercial hydrophobic SiO₂ coatings (PS1, PST1, C4S1, and C4ST1) exhibited hydrophobic surfaces and presented contact angles larger than 100°. The results indicate that the hydrophilic coated surfaces can be changed to hydrophobic by including a hydrophobic silica layer in between TiO₂ layer and cementitious substrate. The ability to achieve surface hydrophobicity lends this TiO₂-SiO₂ nanoparticle-modified coatings to broad applications. For example, in repair applications, hydrophobic coatings are more favorable since it could help prevent water from penetrating into concrete, potentially avoiding future repairs in the same area.

The inclusion of a silica layer also affects the bond strength between coating and cementitious materials. Bonding between coatings and cementitious substrates was evaluated by micrographs obtained after the adhesion tests (Figure 3). Coated cementitious materials with lab-produced hydrophilic SiO₂ interlayer, with or without a titania layer (PS2, PST2, C4S2, and C4ST2), show the coatings can be easily peeled off during the cut without damaging the surfaces of cementitious substrates. Similar observations are made from samples only coated with TiO₂ layers (PT and C4T). This result indicates a weak bond between these coatings and cementitious substrates. In contrast, the surfaces of samples coated with commercial hydrophobic silica layer (PS1, PST1, C4S1, and C4ST1), are irregular and rough during the cut. This result indicates a strong bonding between coatings and cementitious substrates as the damage occurs in the cementitious substrate when peeling off the coatings. This strong bond performance appears to be related to the hydrophobicity or other characteristics of the commercially produced silica layer, since the cementitious substrate did not bond as well to the lab-produced hydrophobic silica-based coating. Further work, including the characterization of commercial SiO₂ sol-gel suspension, is needed to understand the underlying mechanism for this bonding behavior. It should be noted that for coated concrete infrastructure that is subjected to abrasion, a strong bond between coating and cementitious substrate is preferable.

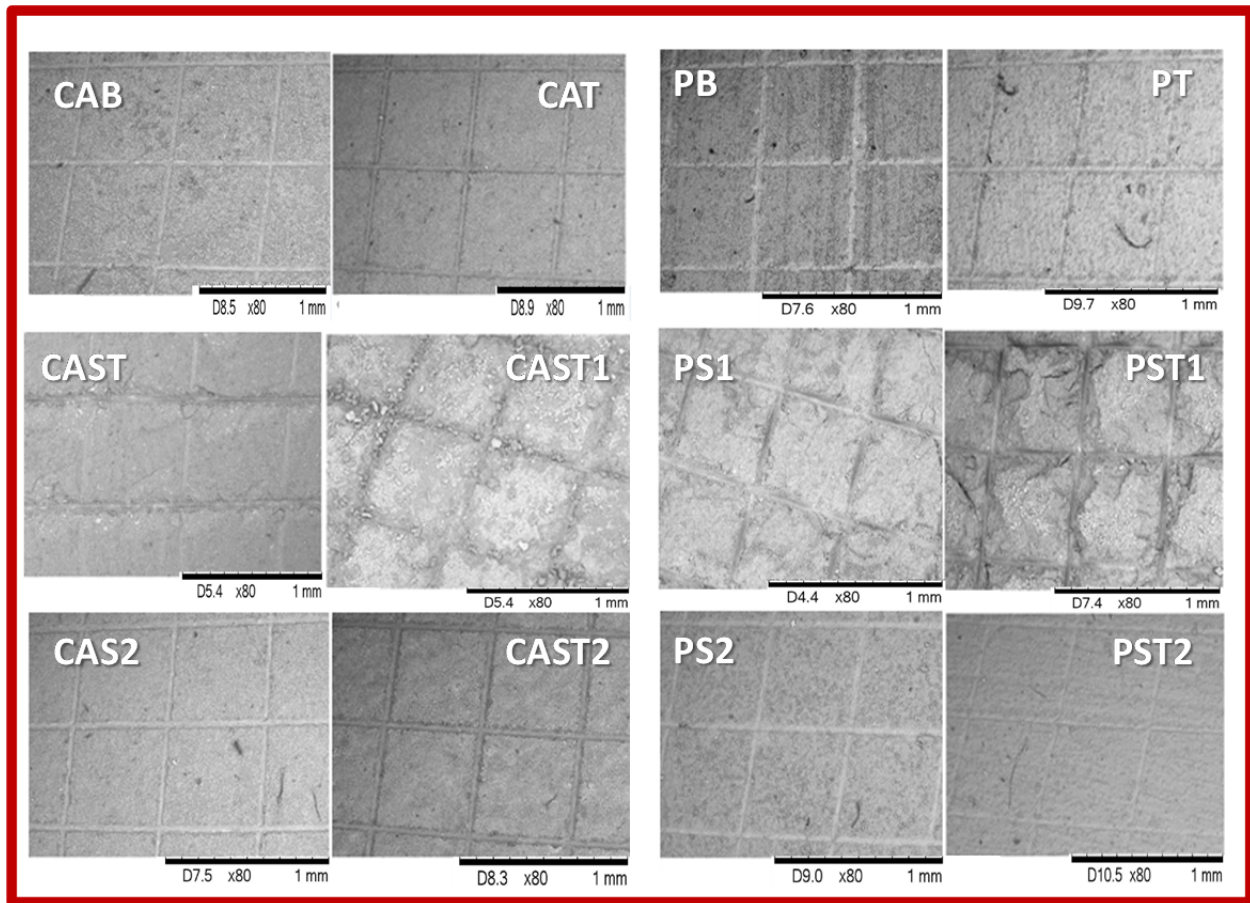


FIGURE 3 - MICROGRAPH OF ADHESION TESTS.

NO_x photo-degradation

The results of the NO_x photo-degradation test along the radiation period are shown in Figure 4 and the photo-degradation efficiencies are summarized in Table 2. The photocatalytic cementitious materials, which contains TiO₂ layer, have shown an instantaneous drop of NO_x concentration upon initial UV light illumination. The photo-degradation of NO_x continued throughout the 5-hour test period, and when the UV light was off, NO_x concentration recovered to the initial level, as expected. The NO_x photo-degradation is believed to be a two-step process, where NO_x is first converted to nitrite and nitrate ions and then the ions are bound with cementitious substrate. Therefore, as mentioned in the introduction, the microstructure of cementitious substrate can affect NO_x photo-degradation through the second step.

In general, the OPC-based photocatalytic cementitious materials (i.e. PT, PST1 and PST2) have NO_x photo-degradation efficiency of 65%, 52% and 60%, respectively, while the CAC-based ones (i.e. C4T, C4ST1 and C4ST2) have 50%, 32% and 40%, respectively. The order of photocatalytic efficiency is: PT>PST2>PST1 for OPC samples and C4T>C4ST2>C4ST1 for CAC samples. The higher NO_x photo-degradation efficiency found in OPC based photocatalytic cementitious materials could be related to the presence of calcium silicate hydrates (C-S-H). C-S-H has a very high surface area (in the range of 10's to 100's of m²/g (5425's to 54250's yard² / lb)³⁸), has a variable composition, and is structurally amorphous to semi-crystalline. This phase is a product of alite (C₃S) and belite (C₂S) hydration, and its complex structure is believed to participate in the adsorption of NO_x oxidized products¹. Based on the characterization study, OPC has a higher SiO₂ and CaO content (Table 1), compared to CAC and shows a more uniform pore size distribution (Figure 1). It is proposed that the presence of C-S-H in hydrated OPC contributes largely in binding the photocatalytic products from NO_x degradation and hence results in a higher NO_x photo-degradation efficiency.

It was also observed that for both OPC and CAC based photocatalytic cementitious materials, the inclusion of SiO_2 layers reduced the NO_x photo-degradation efficiency. Since the SiO_2 layer was applied in between TiO_2 layer and cementitious substrate, it could interrupt NO_x from participating in the near surface reaction of cementitious substrates and hence reduced the NO_x photo-degradation efficiency. For example, the acidity of SiO_2 layer with pH of 2.5-3.0 could interact with the near surface C-S-H and calcium hydroxides, as a result affect the NO_x binding and its photo-degradation efficiency. Therefore, the photocatalytic performance of TiO_2 - SiO_2 composite coating could be compromised by the interruption between coating and cementitious substrate. Comparing S1 and S2, the hydrophobic S2 layer further worsens the NO_x photo-degradation efficiency. This may be due to the hydrophobicity of S2 layer and the chemicals that were used to create a strong bond between coating and cementitious substrate have an even stronger impact on the interruption of the NO_x near surface reaction. Therefore, caution should be made when applying the silica layer to alter the hydrophobicity of coated surface and to enhance the bond strength.

The long-term NO_x photo-degradation was examined by a two-cycle test with each cycle having a consecutive 5-hour NO_x and UV light exposure followed by a 12-hour break. Only TiO_2 coated photocatalytic cementitious materials (PT and C4T) were selected for the tests. The results are shown in Figures 5. Again, the OPC based photocatalytic cementitious material (PT) exhibited a higher NO_x photo-degradation efficiency than the CAC (C4T). A trend in reduced NO_x photo-degradation was observed during the given cycles. It suggests that the photocatalytic cementitious materials have limited capacity of NO_x photo-degradation if the external environmental conditions keep the same.

The NO_x photo-degradation tests support the hypothesis that the NO_x photo-degradation efficiency not only depends on the photocatalytic activity of the coatings, but also on the characteristics of the cementitious substrates. Therefore, it is critical to understand what characteristics of cementitious materials are responsible for NO_x photo-degradation, such as the hydrated cement phases, to optimize the design of cementitious substrate for maximizing NO_x photo-degradation efficiency.

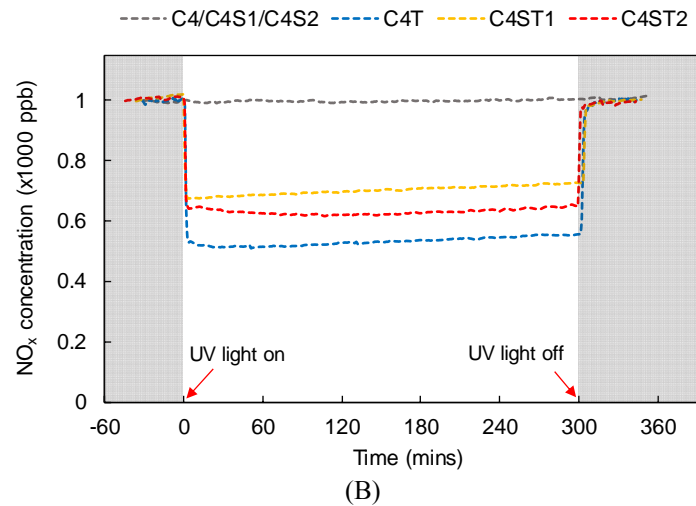
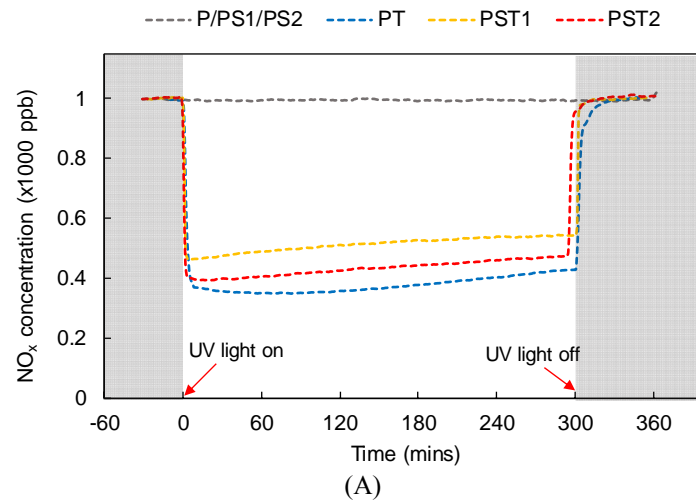


FIGURE 4 - NO_x PHOTO-DEGRADATION RESULT (A) OPC (B) CAC.

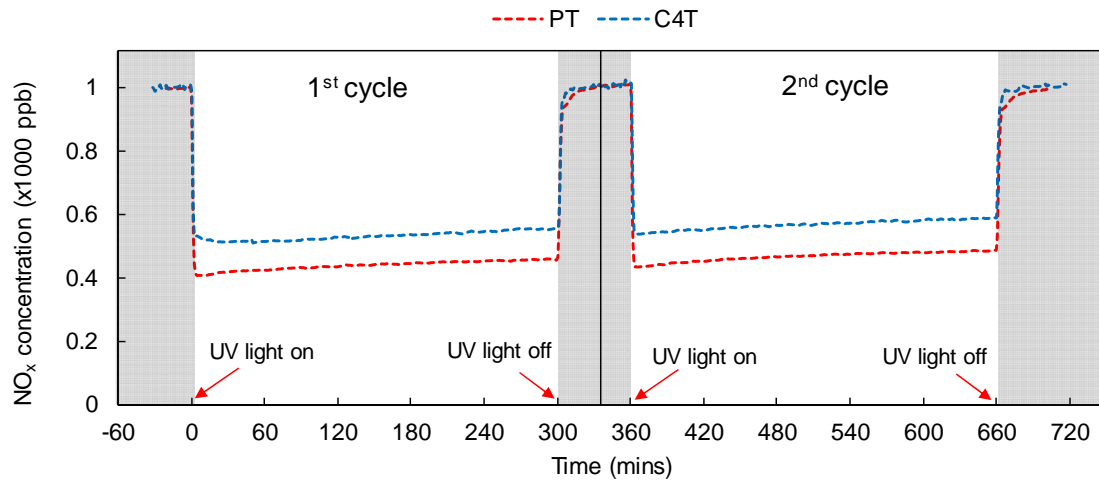


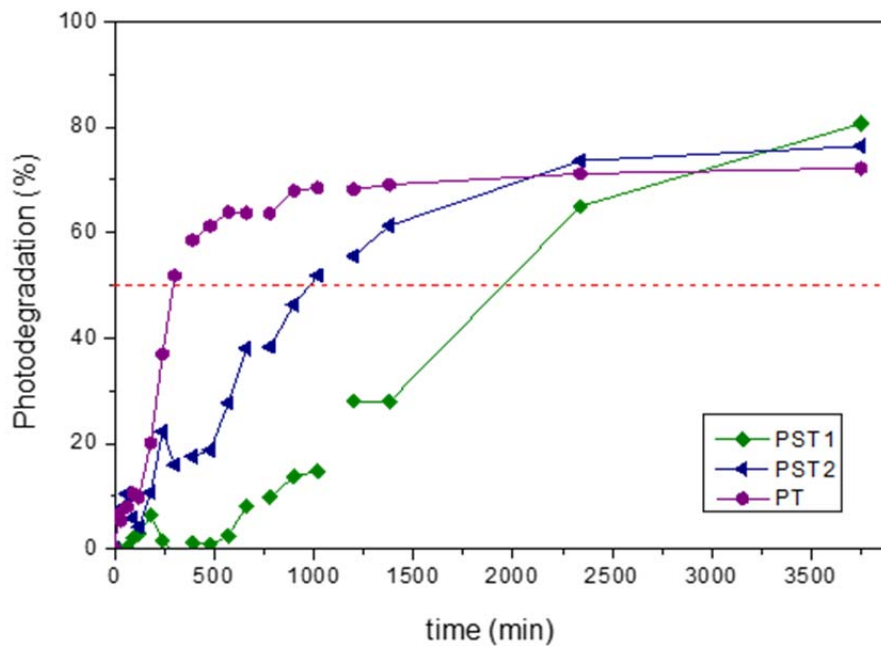
FIGURE 5 - NO_x PHOTO-DEGRADATION – TWO CYCLE TEST.

Methylene Blue (MB) photo-degradation

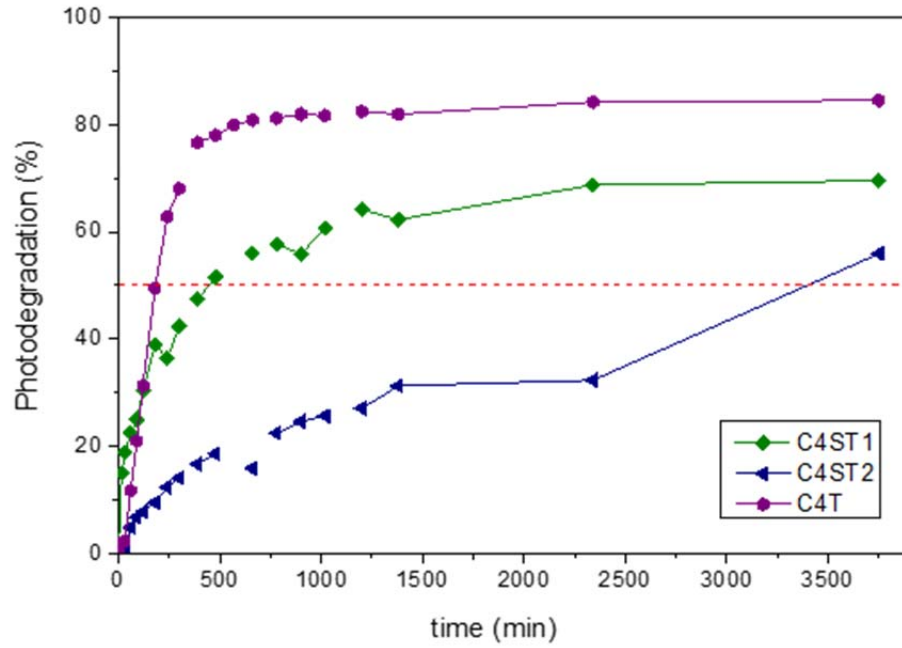
Researchers have brought up concerns about the validity of the MB photo-degradation test that is sensitized by TiO_2 , especially in the presence of oxygen^{39,40}. However, its application in photocatalytic cementitious materials still can provide useful insights^{25,41}, in particular the correlation between MB photo-degradation and photocatalytic self-cleaning behavior. In this study, it was observed that cementitious materials with a TiO_2 layer show a significant MB photo-degradation while the ones without TiO_2 show unmeasurable MB photo-degradation. This evidence suggests that the coatings containing TiO_2 promote the photocatalytic activity and hence increase the rate of MB photo-degradation.

The results of the MB photo-degradation for photocatalytic cementitious materials along with the radiation time are shown in Figure 6. The time to achieve 50 % MB dye bleaching ($t_{1/2}$) are indicated by the red dashed line in Figure 6 and are summarized in Table 2. For both OPC and CAC samples, the samples with only TiO_2 layers present faster 50 % MB dye bleaching (lower value of $t_{1/2}$) than samples with TiO_2 - SiO_2 layers. This result coincides with the findings from the NO_x photo-degradation tests and indicates that the inclusion of silica layers may affect the interaction between coatings and cementitious substrates, hence reduces the MB photo-degradation efficiency. However, the cementitious substrate seems to play a less important role in the MB photo-degradation, which indicates the MB photo-degradation could largely depend on the photocatalytic performance of the coatings.

Moreover, caution should be taken when translating this experiment to real world self-cleaning applications since other factors such as a high humidity and pH can also affect the photocatalytic performance⁴².



(A)



(B)

FIGURE 6 - MB DEGRADATION: (A) OPC AND (B) CAC.

CONCLUSION AND RECOMMENDATION

This study examines the photocatalytic performance of titania and silica (TiO_2 and SiO_2) nanoparticle-modified coatings for cementitious materials. Portland cement (OPC) and calcium aluminate cement (CAC) were used to prepare the cementitious substrates. The substrates were coated each with a lab-produced TiO_2 (T), a commercial hydrophobic SiO_2 (S1), and a lab-produced hydrophilic SiO_2 (S2). Based on the characterization studies and photocatalytic tests, the following conclusions can be drawn:

1. Based on the results of microstructural characterization, the coatings have insignificant effect on the microstructural features of OPC cementitious materials but have effect on CAC samples, especially on the pores of 200-300 nm in diameter.
2. The results of wettability test show that the composite coatings that contain hydrophobic SiO_2 affect the interactions of coated surfaces with water.
3. The results of adhesion test indicate that the coated cementitious materials with commercial hydrophobic SiO_2 layer show the strongest bonding to the substrates.
4. In examining the NO_x and MB photo-degradation, the cementitious substrates coated only by TiO_2 (PT and C4T) exhibit higher efficiencies of both NO_x photo-degradation and MB photo-degradation. The inclusion of SiO_2 layers seems to reduce the photocatalytic performance of coated cementitious materials, especially the ones containing commercial SiO_2 layers. The results of MB photo-degradation tests suggest that the cementitious substrates may have less impact on photocatalytic performance.
5. In comparing between the two cements, OPC-based cementitious materials show higher photocatalytic efficiencies than CAC-based ones. It is proposed that the higher efficiency could be attributed to the finer and more uniform porosity in OPC-based cementitious materials, as well as the presence of high-surface area calcium silicate hydrates (C-S-H).
6. For long-term photocatalytic performance, the results of NO_x photo-degradation in the two-cycle tests for both OPC and CAC photo-cements are consistent with the results found in single cycle tests. It is also suggested that the photocatalytic cementitious materials have limited capacity of NO_x photo-degradation if the external environmental conditions remain the same.

For selecting or designing coatings, it is important to consider the following three factors – the bond strength between the coating and the cementitious substrate, the desired coated surface interaction with water (i.e. hydrophilicity and hydrophobicity), and the photocatalytic performance. For example, if the coating is used to repair pavement surface that is subjected to abrasion, a strong bond and hydrophobicity are preferable. Therefore, it is recommended to include the commercial hydrophobic SiO_2 to improve the bonding performance and to achieve the hydrophobicity. If the coating is used to remove NO_x and clean a surface, then a higher photocatalytic performance is more desirable. In this case, SiO_2 layer should be excluded to maximize the material's photocatalytic efficiency.

ACKNOWLEDGEMENTS

This work is supported by the Spanish Plan Nacional de I+D+i through the project CTM2015-64895-R and National Science Foundation under Grant No. CMMI-1362843. The authors would like to thank Spanish Ministry of Education, Culture and Sports, for “Salvador de Madariaga” program in foreign countries (Ref. PRX14/00237). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Spanish Plan Nacional de I+D+i or the National Science Foundation.

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