Improving the optical-radiative properties of TiO₂ containing coatings – a side effect of air purification

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ABSTRACT

A manifold positive contribution to climate change mitigation and in the improvement of air quality of built environments can be provided by the use of titanium dioxide (TiO_2), also – but not exclusively – as coating for building envelope materials, to spread its beneficial effect on the largest surface area possible. The benefits in applying TiO_2 coatings –containing in particular the anatase phase – rely, first of all, on the UV-activated photocatalytic degradation of pollutants mediated by it, which can mitigate pollution arising from industrial sources, heating and transportation. Moreover, changes in wettability upon UV irradiation lead to a superhydrophilic state which, coupled with photocatalysis, results in the so called self-cleaning effect, allowing materials to retain a cleaner and more reflective surface over time. Reducing the impact of aging on the optical-radiative performance of built environment surfaces has a strong influence on the thermal comfort and energy consumption of buildings.

Here we present a novel effect observed on long-term durability investigations of commercial siloxane paints containing anatase nanoparticles: an increase in reflectance in the near infrared (NIR) wavelength range upon material aging. This could open the door for HNO_3 treatment of TiO_2 as a method to boost the self-cleaning efficiency and reflectance of surfaces for building, construction and solar technologies.

Keywords: titanium dioxide, self-cleaning, solar technologies, near infrared, reflectance

1 INTRODUCTION

The development of photoactive materials with self-cleaning and depolluting qualities is a hot topic in materials science, given their impact on several technologies, in a wide range of contexts of applications. Anatase phase titanium dioxide (TiO_2) is the largest used photocatalyst, with increasing applications ranging from air quality control to renewable energies, to green building materials for zero energy communities [1-3]. Titanium dioxide (TiO_2) finds applications several solar technologies: in dye sensitized solar cells, as photocatalyst for water and air purification, and as self-cleaning coating. Various commercial products integrate TiO_2 in building materials in order to spread its beneficial effect on the largest surface area possible [4,5]. With its high refractive index, rutile TiO_2 is the largest used white pigment, but it is partially transmissive in the near infrared wavelength range, which negatively affects solar reflectance.

TiO_2 in the anatase crystal phase can be activated by UV light, producing different effects, first of all the photocatalytic degradation of pollutants that come in contact with its surface – either in gas or liquid phase, which can mitigate pollution arising from industrial sources, heating and transportation [2]. Degradable pollutants are both organic – industrial wastewaters, volatile organic compounds (VOCs) from exhausts, combustion gases, etc. – or inorganic, mostly referring to nitrogen oxides [6,7]. Furthermore, wettability also changes under UV radiation, with the onset of a superhydrophilic state: this, together with photocatalytic degradation of contaminants, results in self-cleaning, i.e., atmospheric contaminants and soot are partially photomineralized and subsequently washed away by water, provided for instanece by rain, allowing materials to retain a cleaner and more reflective surface over time [8,9]. This reduces the impact of aging on optical-radiative performances of the surfaces that contain TiO_2, on account of a prolonged maintaining of a clear color over time, with limited darkening – and thus reduced reflectane – during the materials lifetime [10,11]. This is exploited not only in the built environment, since it influences the thermal comfort and energy consumption of buildings and therefore the urban microclimate, but also in photovoltaics, where a clear surface better absorbs solar light and is less overheated during hot days, with lower power losses [12,13].

Here we present a novel effect of anatase phase TiO$_2$, which we first noticed during long-term environmental [10] and laboratory accelerated exposure campaigns [14]: an increase in reflectance in the near infrared (NIR) wavelength range upon material aging. This effect is here reproduced in laboratory, in order to identify the responsible mechanisms.

2   EXPERIMENTAL

2.1   Materials preparation

Two sets of commercial materials were used in outdoor long-term exposure: one focused on fiber-reinforced mortars for pre-cast thermally insulated panels (by PIZ SpA) [10], while the other considered polyester-reinforced bitumen roofing membranes (by Index SpA). The latter material was used in laboratory tests here described as well, therefore deserves better description. The bitumen membrane was coated with a water-based siloxane paint, with either standard composition (containing TiO$_2$ white pigments in rutile crystal phase, 300 nm minimum size) or photoactive one (same pigmentary rutile plus anatase TiO$_2$ with 15 nm particle dimension). Samples were cut in 10 cm x 10 cm squares from a membrane sheet 0.5 cm thick and subjected to outdoor exposure for two years. For laboratory investigations smaller samples 4 cm x 4 cm were used.

2.2   Outdoor exposure

The mortars and membranes were exposed to the polluted urban atmosphere of Milan, Italy, for a period of at least 2 years. Outdoor exposure started in Milan in April 2012, and is still running in the case of membranes, with three replicates per product for each exposure condition. Fiber-reinforced mortars were vertically exposed, facing north and south. The roofing membranes were exposed low sloped [15]. The solar spectral reflectance was characterized for unexposed samples, and each six months; here we report the results after two years. Measurements were carried out between 300 and 2500 nm, with a spectral resolution of 5 nm, with a Perkin Elmer Lambda 950 spectrometer, equipped with a 150 mm integrating sphere. Just the central portion of each sample was monitored.

Although we observed an increase in NIR reflectance both on mortars and on membranes, we will focus on the latter materials, which are of easier handling for the following laboratory tests.

2.3   Laboratory tests

We evaluated the response of membranes to contact with possible pollutants deriving from atmospheric pollution. Since the NIR increase was observed only on materials containing photoactive TiO$_2$, no direct pollutant was taken into account, but only degradation products of possible pollutants. Moreover, no organic contaminant was considered, since they are already known to decrease reflectance, rather than increasing it.

Samples were immersed in diluted acids (sulfuric acid and nitric acid, concentrations from 0.1 to 1%), in a neutral mixture of nitrates and carbonates (1%) and in tap water. These solutions were representative of the reaction products that may derive from the photocatalytic degradation of NOx and SOx in the atmosphere, while water was used as control to assess the influence of sole wetting on the materials optical properties. UV-Vis-NIR measurements were performed as described in the outdoor exposure section, with the difference that two non-overlapping spots per sample were measured.

Membranes characterization also included X-ray diffraction (XRD) to evaluate crystal structures and chemical composition of the materials present on the membrane before and after immersion. A Philips PW 1830-Cu Kα radiation instrument was employed (40 kV applied tension, 0.5°/min scan rate).

Afterwards, the best candidate solutions were used to assess the effect of immersion on the sole TiO$_2$ powders, in order to confirm that the source of these reflectance contributions is TiO$_2$ itself and not other materials contained in the membrane. To meet this aim, AEROXIDE® TiO$_2$ P25 powders were used, as representative of a standard material commonly utilized in studies on titanium dioxide photoinduced properties. 1 g of powders was mixed with 3 ml of the chosen solution and dried on a hot plate at 50°C, then deposited on a transparent polyester sheet for optical characterization.

3   RESULTS

3.1   Outdoor exposure

Figure 1 reports the UV-Vis-NIR reflectance of a membrane not containing nanometric anatase TiO$_2$ (standard formulation) before and after 2 years of exposure to the outdoor atmosphere, and that of one containing the photocatalytic admixture. First of all, it is clear that all membranes lose a portion of their Vis reflectance, expecially in the blue region of light, which causes a visible surface yellowing. Moreover, in the NIR range all membranes undergo a decrease in reflectance, which is different in the two cases: on standard ones the whole range is interested by a reduction in reflectance, while on anatase containing ones at light radiation higher than 1500 nm an inversion is observed, and NIR reflectance increases with aging. This is a countertrend with respect to what we expected from experience, and from results obtained on standard membranes. The same behavior was observed on mortars (data not shown).
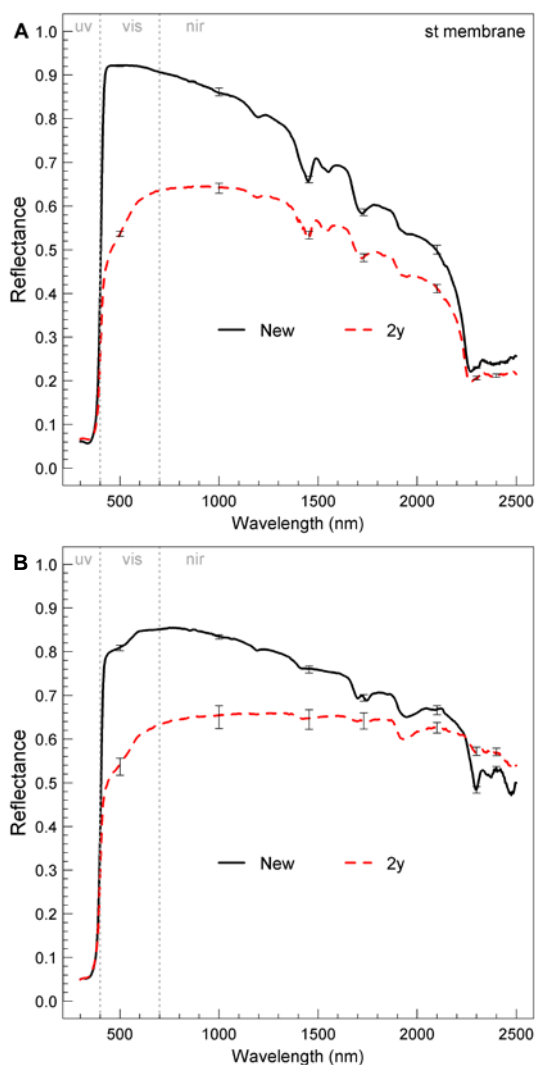
Figure 1: Reflectance before and after 2 years of outdoor exposure of A) standard membranes and B) membranes containing photoactive TiO_2.

3.2 Laboratory tests

After these observations, as already described in the experimental section, we tried to reproduce this behavior in laboratory by immersing the membranes in solutions representing the reaction products of possible photocatalytic reactions. No pollutant pre-existing in the atmosphere was taken into account, as it would have modified also the optical properties of standard membranes.

Pristine membranes were immersed for 24 h in diluted HNO_3, H_2SO_4 or tap water. A nitrates plus carbonates solution with neutral pH was also considered, but did not give positive results. Sulfuric acid was also discarded after first tests; in fact, although the desired effect was actually obtained, the presence of sulfuric acid also damaged strongly the membrane surface, causing the appearance of cracks in the siloxane paint and a relevant yellowing.

By immersion in nitric acid with 0.1% concentration: reflectance decreased from low wavelengths until approximately 800 nm – i.e., in the visible range, while in NIR it increased with respect to the original membrane optical response, therefore reproducing the desired behavior observed in natural exposure. The membrane compositin was examined by XRD, showing a decrease in the content of carbonates after immersion in acid (Figure 2). This is not surprising, since carbonates are soluble in acid environments, but this could not be the source of the observed optical response since carbonates are highly reflective, thus their disappearance would rather decrease reflectance. No other alteration was noticed.
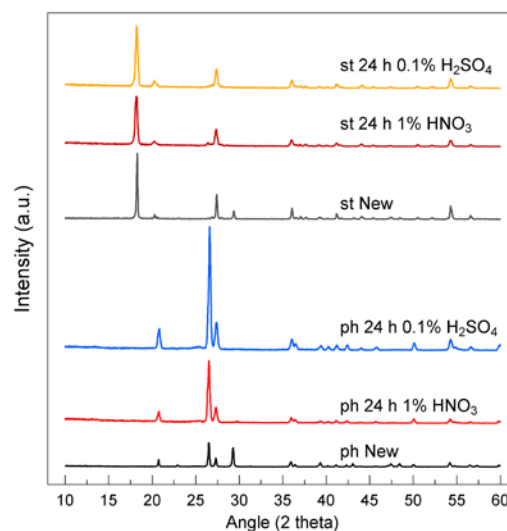

Figure 2: XRD of standard (st) or photoactive (ph) membranes before (new) and after immersion in HNO_3 or in H_2SO_4.

As a consequence, we ascribed the alteration in NIR reflectance to TiO_2 itself. Therefore we repeated immersion experiments in nitric acid (and in water as control experiment) on commercial TiO_2 nanopowders, instead of using a complex commercial material, to isolate the response of TiO_2 to the acid immersion: results are reported in Figure 3. An analogous increase in NIR reflectance was seen, which was not noticed when immersing the powders in simple water. Therefore, we could prove that TiO_2 itself is responsible for the optical modification.

Powders were then observed with SEM but no alteration of any tipe was found to the particles morphology or dimension (data not shown). On the contrary, a large effect on crystallinity was observed by XRD: in fact, TiO_2 nanopowders present a smaller peak of both anatase and rutile, together with a peak broadening, meaning that the powders crystallinity is decreased and crystal size is also decreased (Figure 4).
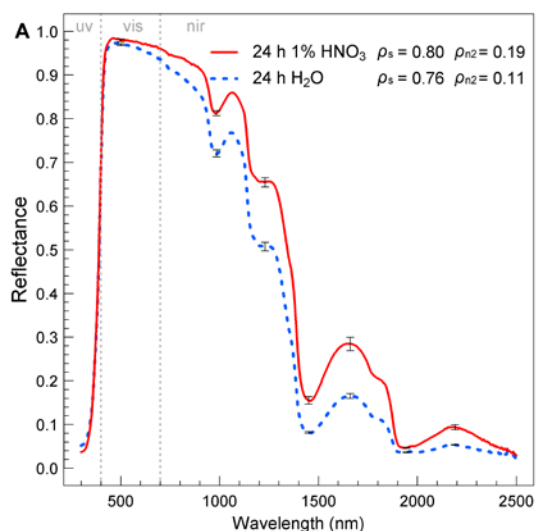
Figure 3: Reflectance of TiO$_2$ P25 nanopowders before and after 24 h immersion in nitric acid or in water.
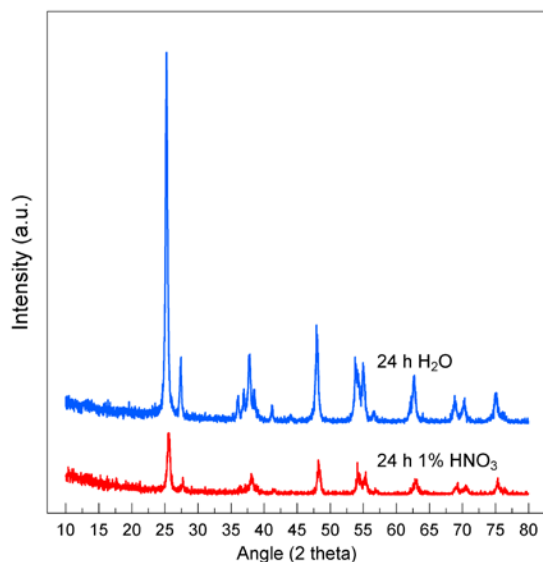

Figure 4: XRD of TiO$_2$ P25 nanopowders before and after 24 h immersion in nitric acid or in water.

The following reaction mechanism was hypothesized to explain the optical variations observed on anatase TiO$_2$ in presence of HNO$_3$ on its surface. Acidity causes an increase in surface area due to some roughening, together with large chemical effects: hydroxylation, protonation, adsorption of NO$_3^-$, increase in Ti^{3+} surface defects. Structural variations are also caused, with the partial degradation of TiO$_2$ crystal structure, as revealed by XRD. Such effects may yield to higher optical density, and therefore reduce transmittance and increase backscattering.

4   CONCLUSION

We here demonstrated how the contact with nitric acid may modifythe optical properties of TiO$_2$ nanopowders, increasing ist reflectance in the NIR range. These findings open the door for HNO$_3$ treatment of TiO$_2$ as a method to boost the self-cleaning efficiency of superhydrophilic surfaces, as well as to improve the optical-radiative properties of TiO$_2$ coatings and admixtures for improved self-cleaning efficiency and surface reflectance of surfaces for building, construction and solar technologies.

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