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Self-cleaning building materials: The multifaceted effects of titanium dioxide

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HIGHLIGHTS

- We treated anatase-rutile nano-powders with HNO_3 or H_2SO_4.
- HNO_3 decreases crystallinity and photoactivity (prevented by neutralization).
- Photoactivity and crystallinity are unaffected by H_2SO_4.
- H_2SO_4 increases the reflectance (1500–2500 nm) of paints with treated TiO_2.
- This treatment can improve the performance over time of TiO_2 added materials.

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ABSTRACT

The physical integrity and photocatalytic performance of titanium dioxide (TiO_2) deteriorate with aging. Here we propose a pre-treatment with nitric or sulfuric acid of commercial TiO_2 nanopowders used in coating, mortars, or paints. The diffuse reflectance is increased between 1500 and 2500 nm by 0.04 and 0.06, respectively, with nitric and sulfuric acid (unaffected by neutralization). Nitric acid causes a decrease in crystallinity and photocatalytic activity, which drops by almost 20%; this drawback is prevented by post-treatment neutralization, which allows to recover initial photocatalytic efficiency and even increase it. Treatment with sulfuric acid shows no significant effect on photoactivity, instead.

1. Introduction

Well before the discovery of its photocatalytic properties, titanium dioxide (TiO_2) has been used massively as a white pigment in textiles and paints [1], where in fact traces of its reactivity were perceived in the form of alterations of supporting materials – such as degradation of paints and fabrics, or bleaching of dyes. Still, the first scientific work on this subject dates back only to 1929 [2], suggesting an active role of TiO_2 in the fading of paints. Eventually, the presence of active oxygen species detected on TiO_2 surface was identified as cause of the photobleaching of dyes in presence of UV-irradiated TiO_2 in the late 1930s [3], but the mechanisms of heterogeneous photocatalysis in presence of metal oxides were only described in the second half of XX century, and in the 1970s proofs of TiO_2 photocatalytic activity were published [4,5]. Finally, in the 1990s, the self-cleaning effect of TiO_2-containing materials was revealed [6]. Since then, large attention has been dedicated to the integration of this oxide in building materials, with possible positive consequences on the quality of the surrounding environment – i.e., cleaner air – and on the reduction of maintenance costs [7–9]. Several buildings have been designed to take advantage of TiO_2 photocatalytic and self-cleaning activity, such as the Marunouchi Building (or Marubiru), in Tokyo, opened in 2002, one of the first buildings featuring self-cleaning window glasses, the jubilee church Dives in Misericordia, built in Rome in 2003, the Hospital Manuel Gea Gonzalez (Mexico City) completed in 2013, or the Italian pavilion at the Milano Expo 2015 Universal Exposition.

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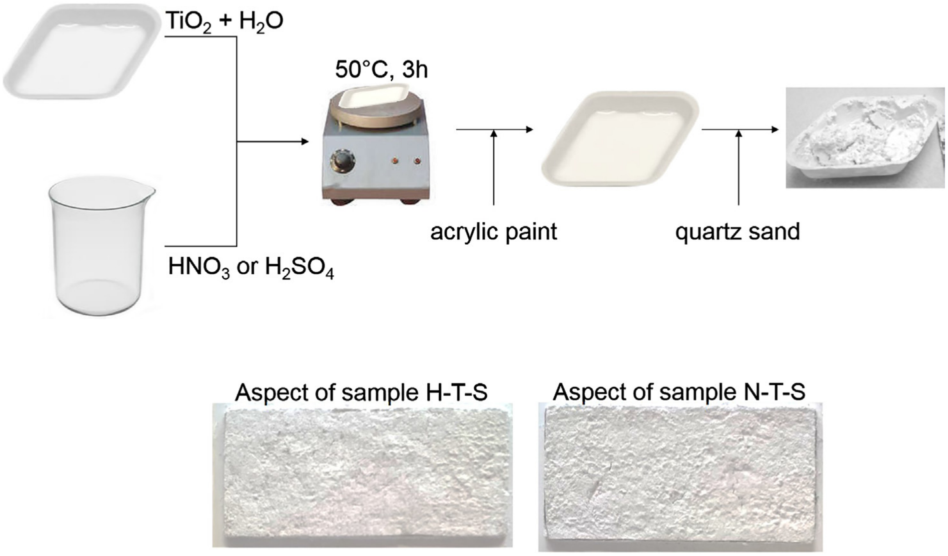

Fig. 1. Samples preparation steps and illustrative samples pictures.

The applications of TiO_2 containing building materials have been widening in the last years, going from the obtaining of self-cleaning façades [10–14] or roads [15–19] with added antipollution effects [20–23] to the development of preservation treatments for architectural heritage, especially in stone [24–28]. While the mechanisms of photocatalytic and self-cleaning activity have been long studied, together with the development of materials with improved photoactivated performance, their durability and the appraisal of the photoactivated effects over time, in real working conditions, remain only marginally treated. This is particularly true in the case of building materials used outdoors, where environmental agents such as rain, wind, pollution and microbiological growth may gradually deactivate the TiO_2 component, or cause the degradation of the whole material by erosion or other physical mechanisms [11,12,29–32].

In more recent times, a further aspect related to the presence of TiO_2 has been analyzed, which refers to its potential as cool pigment [33–36]. Cool surfaces do not overheat under the sun as they present a high solar reflectance, namely the ratio of reflected to incident solar radiation, and high thermal emittance, namely the ratio of emitted thermal radiation to that emitted by a black body. The use of cool materials for built surfaces, especially for roofing, minimizes the solar heat gains in buildings, reducing the cooling energy needs and peak power demand, and mitigate the local climate, reducing the heat released in the urban environment [37–41]. Since weathering and soiling can greatly reduce these benefits [41–44], recent building energy regulations, such as the Title 24 of the State of California, prescribe that non-residential roofs shall have a minimum aged solar reflectance (after three years) of 0.63 [45]. We recently demonstrated that anatase added materials suffer a less pronounced drop in solar reflectance upon environmental exposure (0.19 instead of 0.26, after two years) [35]. In the second portion of the near-infrared wavelength range, namely between 1500 nm and 2500 nm, as aging proceeds, the reflectance increases even in comparison to the freshly prepared material, which was ascribed to the material photocatalytic NOx degradation, responsible for the formation of nitric acid that alters the optical properties of the TiO_2 nanoparticles (NPs) present in the material [29,35].

This article presents a change in perspective with respect to the issue of self-cleaning TiO_2-contaning materials with high solar reflectance. In fact, in the present study, TiO_2 NPs are modified to enhance their optical properties before adding them to the building material of interest, in this case, an acrylic paint. Two possible acid treatments are employed to this aim, i.e., with diluted nitric acid or sulfuric acid. Moreover, since these modified powders are envisioned as admixtures to construction materials (mortars, paints), with related handling issues, a final step of powders neutralization is also proposed and evaluated, to check whether modifications obtained by acid treatment are maintained also in neutralized powders. The TiO_2-containing paint was then characterized from the point of view of its optical properties as well as its photocatalytic performance.

2. Experimental

2.1. Samples preparation

The passages followed to prepare TiO_2 containing samples are summarized in Fig. 1. The photocatalyst used in the preparation and study of paint samples is AEROXIDE® TiO_2 P25 by Evonik Industries. It contains a combination of anatase and rutile of about 80–20% with purity >99.5% and specific surface area of 35–65 m^2/g. 1 g of nanoparticles was first dispersed in 4 g of distilled water before incorporation into the paint, producing a suspension of TiO_2 and distilled water with [1:4] ratio. Although an ultrasonic bath was used, the suspension still contained agglomerated nanoparticles and had a slightly milky appearance. Nitric acid and sulfuric acid were diluted (0.5% by weight for HNO_3 and 0.1% for H_2SO_4) and 5 g of solution were added to the aqueous TiO_2 suspension to perform an acid treatment of the NPs, which was shown to produce positive effects on their NIR reflectance [35]. A new solution was then obtained, containing 10% by weight of TiO_2. The mixture was then evaporated on an electric plate at approximately 50 °C, to reduce the water content before mixing with the paint, giving a total duration of the NPs-acid contact of 3 h; the final TiO_2 concentration was 33.3% (TiO_2:solvent in a ratio 1:2). In a latter formulation, after this interaction time and before incorporation in the paint, the mixture was also neutralized by adding a stoichiometric quantity of NaOH aqueous solution. Table 1 reports the sample labels as a function of the TiO_2 nanoparticles treatment. Each composition was used to produce at least two samples to be used in optical measurements and two samples to be used in photocatalysis tests.