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Below room temperature: How the photocatalytic activity of dense and mesoporous TiO_2 coatings is affected

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ABSTRACT

Different parameters such as morphology, porosity, crystalline phase or doping agents affect the self-cleaning performance of photocatalytic TiO_2-based coatings. However, also environmental conditions have been found to play a major role on the photocatalytic self-cleaning property. Substrate temperature is a significant environmental variable that can drastically affect this process. This variable becomes of great importance especially for outdoor applications: many self-cleaning photocatalytic materials have been designed to be exposed to outdoor environments and consequently, can be exposed to variable temperatures depending on the season of the year and the typical weather of the geographical zone. Thus, understanding the influence of the most common outdoor temperatures on the self-cleaning performance of TiO_2-based coatings is essential for the fabrication of any kind of photocatalytic self-cleaning materials (fabricated by coating technology) that is expected to be subjected to outdoor environments. In this work, the photocatalytic activity was studied by Fourier Transformed Infrared (FTIR) Spectroscopy varying the temperature in the 0 to 30 °C range for dense and mesoporous TiO_2 coatings. The temperature conditions at which these coatings present better performances were identified, providing a deeper insight for the practical application of TiO_2-based self-cleaning coatings.

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1. Introduction

In the past decades, the use of TiO_2-based photocatalysts has attracted the interest of both fundamental science and industrial applications [1]. The properties of TiO_2 can be used to impart the self-cleaning functionality to a variety of materials including tiles, glasses, plastic coatings, panels, wall papers, window blinds, paints, tunnel walls and road-blocks to name a few [1]. The total market for photocatalyst products is forecast to grow during the next five years, and is estimated to be valued at nearly $2.9 billion by 2020 [2]. The overall self-cleaning effect of TiO_2 can be explained by two photochemical phenomena that occur on its surface under illumination: 1) the photoinduced redox reaction of adsorbed substances, and 2) the photoinduced super-hydrophilicity [1]. Degradation of pollutants occurs when TiO_2 is irradiated with ultraviolet light, and holes (h^+) and excited electrons (e^-) are generated. Holes are trapped by hydroxyl groups (OH^-) adsorbed on the surface to generate hydroxyl radicals ($OH^\bullet$), which are powerful oxidizing agents for the degradation of a wide range of organic pollutants [3].

Considering the potentiality of TiO_2 in the building industry, understanding how temperature affects the photocatalytic performance is a relevant task, especially for outdoors environments, were ambient conditions are usually more variable. Temperature is known to influence the reaction pathways and the kinetics of the photo-induced degradation process [4,5] as well as the formation of the super-hydrophilic surface [6], affecting the final self-cleaning performance of TiO_2 photocatalyst. The research in the field of TiO_2 photocatalysis is constantly growing (more than 16,000 papers published only in the last decade) [7] and many building materials that use the photocatalytic technology have been developed for indoor and outdoor applications [1]. However, limited research has been dedicated to the influence of increasing temperature [3–5,8–11] or to the influence of relatively low temperatures (*i.e.* $T \leq 20$ °C) [5,8,11–14]. For the building industry,

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information about the performance of TiO_2-coated construction materials in a wide range of temperatures [15] and using solid pollutants as representative models of stains becomes of great importance: it is expected that these materials will play a major role on the decontamination of the surrounding environment. Examples that can be mentioned are the preservation of the aesthetic image of building materials (e.g. glasses, tiles) in the construction industry and the antibacterial functionality that can be imparted by these coatings on a number objects. In a previous work, it was found by the design of experiments approach that temperature is a significant factor that positively influences the photodegradation of stearic acid (SA) using TiO_2 coatings [5]. Moreover, when combined with variations in the UV incident light (keeping humidity constant), it was observed that the correlation between these factors determines the regime of SA degradation. Since in that work it was found that temperature is a significant variable that affects the photocatalytic activity (PCA) of TiO_2 coatings, in the present work the effect of the most common outdoor temperatures (in Europe) was further investigated, focusing on the differences of microstructures of the investigated coatings. Two TiO_2 coatings with different morphologies were used: (i) a sol-gel derived TiO_2 coating with a dense (or non-porous) morphology, and (ii) an ordered mesoporous TiO_2 coating prepared by evaporation-induced self-assembly (EISA) using triblock non-ionic surfactant (*e.g.* Pluronic F127) as a templating agent. This latter is a high surface area coating with ordered porosity and improved photocatalytic performances over low porous coatings [16]; importantly pristine and doped mesoporous TiO_2 coatings are both considered important self-cleaning materials [17,18].

It is important to emphasize that TiO_2 is a well-known photocatalyst and both dense and mesoporous coatings have been deeply studied. However, most of the reports concerning mesoporous TiO_2 photocatalyst are focused on the synthesis of mesostructures [19], the diffusion of pollutants trough the structure [20], and the influence of crystallinity, pore distribution, pore accessibility and doping on the photocatalytic activity [21]. Thus, there are only few reports of mesoporous TiO_2 photocatalyst that take into account environmental variables such as temperature in the degradation process of solid contaminants. On the other hand, the influence of temperature on the photocatalytic degradation of liquid [11] and gaseous [22] pollutants using dense (or non porous) TiO_2 coatings has been already reported. Although there are some reports in which solid pollutants are used, high ambient temperatures (>20 °C) are usually considered [3,4,9,10,23] and the results are not further compared with TiO_2 coatings of different microstructures. As both temperature and solid pollutant models are of great interest for TiO_2-based self-cleaning building materials, the aim of this work was to evaluate the influence of temperature in the performance of dense and mesoporous TiO_2 coatings using SA in the 0–30 °C range. This could predict the influence of the climate conditions within a vast range of longitudes and altitudes on the self-cleaning properties. Thus, this study provides useful information for a judicious choice of the TiO_2 coating features considering the *temperature working* conditions.

2. Materials and methods

2.1. Synthesis of dense and mesoporous TiO_2 coatings

The sol-gel approach was used for the deposition of TiO_2 coatings due to the versatility towards a number of industrial applications [24]. The synthesis of dense TiO_2 coating was carried out following the optimized sol-gel procedure reported by Costacurta et al. [3]. Briefly, the TiO_2 precursor sol for the deposition of a dense coating was prepared by mixing titanium isopropoxide (98+% ACROS Organics), absolute ethanol (MERCK EMSURE®) and HCl 1M (from 32% EMSURE) in the molar ratios 1:100:0.06; the sol was stirred for 1 h before coating. A silicon wafer, used as substrate, was dip-coated in the fresh sol at 14–15% relative humidity (RH) setting the withdrawal speed at 100 mm min^{-1}. Four layers were deposited; performing a thermal treatment at 100 °C for 10 min and then 250 °C for 30 min after each deposition step. Finally, the temperature was increased up to 500 °C for 3 h to induce the formation of anatase crystals.

The mesoporous TiO_2 coating was prepared using a modified version of the procedure reported by Crepaldi et al. [19]. $TiCl_4$ (≥99.0% FLUKA Analytical) was slowly poured into a mixture of absolute ethanol (MERCK EMSURE®) and tri-block copolymer Pluronic F-127 (SIGMA). Water (18 MΩ) was added dropwise after 5 min of vigorous stirring. The resulting molar ratio was $TiCl_4$:EtOH:H_2O = 1:40:12 and the $TiCl_4$/Pluronic F-127 ratio was 0.006. The coating was deposited at 18–20% RH on a Si substrate setting the dip-coater withdrawal speed at 160 mm min^{-1}. After deposition, the coating was exposed to water vapours for 30 s. The obtained mesoporous coating was maintained at 200 °C for 24 h to stabilize the mesoporous structure and then the temperature was increased up to 500 °C and kept for 3 h to induce the anatase phase formation.

2.2. Coating characterization

Characterization of the coatings was made with the aim of understanding their similarities (both films were based on anatase TiO_2) and differences (dense and mesoporous microstructure), and to further correlate these characteristics with their photocatalytic behaviour at each temperature. Grazing incidence X-ray diffraction (GIXRD) was used to characterize the coatings using a PANAlitycal X'Pert PRO diffractometer with Cu Kα1 radiation. The ordered mesostructured TiO_2 was investigated using synchrotron radiation by small-angle X-ray scattering (SAXS) in grazing incidence mode at the Australian Synchrotron (Melbourne, Australia). The angle of incidence of the beam (λ = 1.54 Å) was set slightly above the critical angle (grazing incidence mode or GISAXS). Two-dimensional patterns were recorded with a CCD detector (Pilatus). Thickness and microstructure were analysed by means of a FEI Nova NanoSEM 450 Field Emission SEM (FEG-SEM), in immersion lens mode. AFM images of the samples were acquired by a Digital Instruments NanoScope 3D in non-contact mode (scan area of 500 nm^2).

2.3. Experimental setup

The photocatalytic reactor consisted in a closed rectangular (45 × 37 × 29 cm) polystyrene container normally used to preserve biological samples with dry ice. A sensor (RS-1365, RS components ltd) was introduced in the reactor and kept 30 mm above the sample holder to monitor the air temperature and air relative humidity in the whole reaction chamber. The light source used was a 365 nm, 15 W, UV lamp (VILBER LOURMAT VL-215 LC). The temperature inside the reactor was adjusted using dry ice/ethylene glycol [25], ice/water, or temperature controlled oil baths. The sample-holder consisted in a Pyrex glass plate that was placed in direct contact with the baths; the samples were kept at 60 mm from the UV lamp. Once the temperature was stabilized inside the reactor and a constant temperature was measured on the sample, the shutter in front of the lamp was opened. Cold baths were replaced every hour making the temperature stable around the set value with a maximum variation of ±2 °C.

2.4. Photocatalytic tests

For all photocatalytic performance measurements, SA was used as model organic molecule because it is stable under UV illumina-

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