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Photo-catalytic efficiency of laboratory made and commercially available ceramic building products

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Abstract

Self-cleaning building products are mainly based on the application of nanotitania onto exposed outdoor surfaces. In order to achieve high self-cleaning efficiency for outdoor applications, it is important that nanotitania is in the form of anatase, and that particle sizes (also in the case of additional thermal treatment) are in the nano-range, so that a large enough specific surface area can be activated. The particle size and the mineralogy of the photocatalytic layers were determined by means of SEM and Raman spectroscopy, respectively.

The self-cleaning efficiency of nanotitania-based material can be evaluated by different methods; in the present paper the suitability of the method based on the discolouration of methylene blue was verified on some samples that were prepared in-lab (through the application of commercially available TiO_2 sol onto a ceramic substrate), as well as on samples of commercially available products.

Keywords: Photo-catalysis; TiO_2; MB discolouration; Raman spectroscopy

1. Introduction

The surfaces of exposed building materials, such as ceramic tiles, roofing tiles, glass, and facades, are exposed to environmental conditions which can result in the depositing of dirt onto them, so that cleaning, which is connected to a high consumption of energy, labor, and detergents, is needed, resulting in high maintenance costs.

In order to reduce costs and improve the long-term esthetic appearance of the exposed surfaces of building materials, nano-TiO_2 coatings, with photocatalytic and hydrophilic properties, can be applied. If TiO_2 is illuminated by UV light, grease and other dirt of organic origin decompose, and when the TiO_2 surface becomes super-hydrophilic, its high affinity for water results in a self-cleaning effect, as rainwater can remove dirt from the surface due to its preferential adsorption [1]. The initial process of photocatalysis consists of the generation of charged carriers, electrons and holes, after the absorption of efficient photon energy ($h\nu \geq E_g = 3.2$ eV) by titania; e^- are the electrons in the conduction band and h^+ are the electron vacancy in the valence band of a semiconductor like TiO_2.

$$TiO_2 + h\nu \rightarrow TiO_2 + h^+ + e^- \quad (1)$$

The separated e^- and h^+ can recombine in bulk or on the particle surface forming $e^- - h^+$ pairs, and causing deactivation of the photocatalytic reaction.

If charge separation is maintained, the e^- and h^+ can migrate to the surface of the TiO_2 particles, where they participate in reactions with adsorbed water and oxygen to form reactive radicals. The latter then react with organic molecules and dirt; the e^- participate in a reaction with an oxidant, i.e. acceptor molecule (oxygen from the air) in order to produce a reduced product (the super-oxide ions $O_2^{\bullet -}$, which are also highly reactive and are able to oxidize organic materials);

$$(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -} \quad (2)$$

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The h^+ (holes) participate in the reaction with the adsorbed donor (water) to produce an oxidized product (the highly reactive hydroxyl radical (•OH));

$$(H_2O \leftrightarrow H^+ + OH^-)_{ads} + h^+ \rightarrow \bullet OH + H^+ \quad (3)$$

Both the super-oxide ions and the hydroxyl radicals then proceed to oxidize the adsorbed organic molecules. In this way, for example, grease and oils can be fully mineralized into carbon dioxide and water [2].

The application of photocatalysts to building products began in the early 1990s. Building products which can be presently upgraded by photocatalytical coatings include: ceramic tiles, glass, panels, soundproofing walls, tunnel walls, road blocks and concrete pavements [3].

Nanotitania can be deposited by different techniques with regard to the final product and its use (e.g. the spray technique, inkjet printing) [4], and is frequently additionally subjected to a high temperature process up to 900 °C in order to improve its adhesion properties [5–7]. Such thermal treatment can significantly influence its photocatalytic efficiency, affecting its two most important parameters. Firstly, if the temperature of fixing is too high, the anatase transforms into rutile which is much less photocatalytically active for outdoor applications (under UV illumination). Secondly, during the heating process, the particles of nanotitania start to grow, which causes a lowering in their specific surface area, and consequently reduces photo-catalytic efficiency [8].

Numerous experimental methods have been developed for the evaluation of the photocatalytic efficiency of the three different phase systems: the gas–solid phase system, the liquid–solid phase system and the solid–solid phase system. Much progress was made in this field by the International Organization for Standardization under technical commitee TC 206 Fine ceramics, which, from 2007 onwards, has published 7 new standards on photocatalytic efficiency [9–15]. Some other such standards are still being developed. Efforts have also been made through the COST 540 action [16] to develop specific methods with high sensitivity; e.g. the decomposition of isopropanol into acetone and further into water and CO_2 [17], or the degradation of terephthalic acid into hydroxyterephthalic acid, which is highly fluorescent and as such can be easily detected by means of HPLC-FLD [18].

Of all the methods, discolouration of methylene blue (MB) dye as a model pollutant is most often used for the testing of materials with self-cleaning properties [9,19–23]. It is based on the monitoring of the discolouration (decomposition) of the MB in de-ionized water when the solution is in contact with the photocatalyst (i.e. a liquid–solid system).

The goal of the work presented in this paper was to prepare photocatalytic samples in the laboratory, and to compare the properties of the nanotitania coatings, after performance of the firing process, with regard to size, mineralogical phase and self-cleaning efficiency, with those of selected commercially available photocatalytic products.

2. Experimental

2.1. Materials and preparation

Ceramic tile samples with titania coatings were prepared in the laboratory from TiO_2 suspensions (1% and 4%) in isopropanol based on Hombikat XXS 100 (Sachtleben Chemie GmbH) sol of anatase of declared size 7 nm. The suspensions were stirred for 24 h at room temperature and then deposited on the ceramic tiles, which had smooth surfaces, by means of a spray technique, at a pressure of 6 bars. The titania films were dried at 100 °C for 30 min, and then fired up to 700 °C and 850 °C at a rate of 100 °C/h, using a dwelling time of 30 min at the selected temperature.

The investigated commercially available samples of ceramic tiles, glass and roofing tiles which were declared to be photo-catalytically efficient were obtained directly from the market.

2.2. Characterization of the samples

The morphology and particle size of the nanotitania coatings were determined by Field Emission-Scanning Electron Microscopy (FE-SEM), using a Supra 35 VP, Carl Zeiss electron microscope. Particle size was determined from SEM micrographs using Image Tool for Windows software (version 2.0).

Raman spectra were recorded in order to determine the mineralogical phase (anataze/rutile) using a LabRam HR800 Raman spectrometer (HORIBA Jobin Yvone) equipped with an Olympus BXFM optical microscope and an air-cooled CCD detector. The samples were excited by the 514.45 nm line of an Argon ion laser operating at a power of 17 mW, using neutral density filters.

2.3. Performance of the photo-catalytic tests

The samples were first pre-irradiated in an irradiation chamber equipped with two parallel UV-A bulbs (40 W, Osram Eversun, $\lambda_{max} = 360$ nm, 10.0 W/m^2) in order to decompose any possibly remaining organic contaminants by photo-catalytic oxidation. A cylindrically shaped glass cell, with an inner diameter of 40 mm, was attached to each sample using silicon glue. Since the substrates tend to adsorb the dye molecules, pre-adsorption of the surface was performed using a 20 μmol/L aqueous methylene blue solution. After the adsorption process of the dye was complete, the adsorption solution was replaced by 40 ml of the test solution (10 μmol/L) and the samples were exposed to UV-A light in the irradiation chamber using Osram Eversun bulbs (40 W, $\lambda_{max} = 360$ nm, 10.0 W/m2). The decomposition rate of the dye under the UV-A light irradiation was determined by measuring its maximum absorption spectrum at 664 nm using a UV/VIS spectrophotometer (Ocean Optics Inc.) every 2 h. The photo-catalytic activity of the TiO_2 was defined as the photo-degradation rate of the dye (i.e. the rate of decrease