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Development of photocatalytic ceramic materials through the deposition of TiO₂ nanoparticles layers

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Abstract

Urbanism and communities centralization enlarges atmospheric pollution that affects both human beings as well as their constructed buildings. Different scientific and technological studies are being conducted, both in academic and construction industry, aiming the development of new construction materials with properties that can decrease visual pollution of cities, reducing also the number of cleanings required.

The present research work aims the study and the production of self-cleaning ceramic surfaces in an economical and viable way without changing aesthetical aspect of material substrates used. The use of TiO₂ nanoparticles (TiO₂-NNPs) represents an attractive way to generate self-cleaning surfaces, therefore promoting the degradation of pollutant agents and reducing cleaning maintenance costs. In order to impart self-cleaning properties to ceramic surfaces, TiO₂-NNPs based layers were deposited on different ceramic material substrates using the dip-coating method. The Photocatalytic activity (degradation of pollutants adsorbed on the surface) of the TiO₂-NNPs based layers was characterized via the decomposition rate of an aqueous solution of Methylene blue (MB) under UV light irradiation. Colourless layers were successfully produced onto gray and white ceramic substrates using this sol-gel technique, without changing their aesthetical appearance. It was observed that the best photocatalytic activity was exhibited by the most porous ceramic substrate (gray); nevertheless, all the TiO₂-NNPs coated ceramic surfaces showed good photocatalytic efficiency.

1. Introduction

The economical growth of countries has been encouraged people's migration from rural to urban neighborhoods toward the enhancement of citizen's quality of life.

However, it is also a known fact that urbanism and communities centralization enlarges atmospheric pollution that affects both human beings as well as their constructed buildings [1]. Nowadays it is essential to plan metropolitan areas with sustainable approaches preserving and/or forecasting green spaces between buildings [2]. Meanwhile, urban populations have been rising, increasing the market need for bigger and comfortable available flats nearby city centers [1]. The construction of taller buildings appeared as a solution and, in fact, a large amount of skyscrapers have been built in the last 10 years. Currently, the façade soiling and staining is a concern given that they represent considerable maintenance costs [3,4]. Being migration a process intrinsically tied with countries economical growth it is important to suppress its negative consequences.

Nanostructured materials will have a tremendous impact in some niche market of construction industry [5]. A lot of scientific and technological studies are being conducted, both in academic and industrial areas, aiming the development of new materials with properties that can decrease visual pollution of cities, reducing also the number of cleanings required.

Heterogeneous photocatalysis come up as a promising and potential technology to be applied for self-cleaning and de-pollution abilities which arise from the photocatalytic properties of materials employed [6]. Some semiconductor materials such as titanium dioxide (TiO_2), when exposed to UV light, act as a catalyst promoting the photodecomposition of organic molecules adsorbed on its surface [7]. This semiconductor material is a target of several research works due to its powerful oxidation strength, chemical stability, non-toxic properties and availability [8,9].

When the surface of titanium dioxide is irradiated with UV light, with energy higher than or equal to its band gap energy ($3.0\text{-}3.2\text{eV}$) – $h\nu \geq E_{\text{gap}}$ – inter band transition is induced, creating photoelectrons (e^-) and photoholes (h^+) [10]. The standard chemical redox reactions involving TiO_2 photocatalysis is well described elsewhere [11,12]. Due to the presence of the band gap energy in semiconductor materials, rapid deactivation of excited electrons and hole pairs (e^-/h^+) is prevented, assuring a sufficient lifetime of (e^-/h^+) pairs so that they can participate in interfacial reactions [13]. Different scientific studies report that titanium dioxide thin films have good photocatalytic activities when (a) there is an efficient photoinduced electron-hole pair generation and (b) there is an efficient charge separation, which, on the other hand, requires the production of crystalline TiO_2 thin films, preferably with anatase phase [14,15]. However, it was also reported that some powders containing both anatase and small amounts of rutile crystalline phases have higher photocatalytic activity than that of pure anatase [16].

There is a wide range of approaches used to deposit TiO_2 layers on glass and polymer substrates such as physical and chemical vapor deposition, sol-gel and dip-coating techniques, among others [17-20]. Sol-gel technique arose as a promising technology to prepare TiO_2 thin films [21-25]. Though, the produced TiO_2 layers are amorphous being necessary an additional heat treatment at a relatively high temperature [26]. Nevertheless, from the industrial point of view, it is crucial the production of crystalline layers at low temperature. Among these deposition techniques, liquid phase deposition techniques such as spin-coating or dip-coating have come to get a particular interest since they can be used to prepare high quality TiO_2 -NNPs based layers, at low production costs and with relatively industrial scaled-up.

The present research work deals with the study of the photocatalytic and self-cleaning properties of TiO_2 -NNPs coated ceramic surfaces obtained via dip-coating method.

2. Experimental details

Production of TiO_2 -NNPs based layers by dip coating

The dip coating technique was used to produce TiO_2 -NNPs based layers on $50 \times 50 \times 10$ mm square ceramic material substrates, provided by Revigres®, (Table 1).

Table 1 - Characteristics of the tested ceramic samples

Sample Code	Characteristics	
	Color	Burnishing
NP-G	gray	not-polished
NP-W	white	not-polished
P-W	white	polished

Commercial TiO_2 -NNPs (Aeroxides® TiO_2 P25 from Evonik industries) with a density of 3.8 g/cm^3 were mixed with distilled water in order to prepare an aqueous solution with a concentration of 0.5 g/L . The solution was then homogenized in a magnetic stirrer during 10 min. In order to produce the final TiO_2 -NNPs suspension, the previous solution was mixed with an anionic self cross-linking resin (PRIMAL™ ECO-934TK from HORQUIM®), which had a pH value of 4.8 and a maximum viscosity of 200 mPa.s .

Then, the 50×50×10 mm square ceramic substrates were dip coated on the suspension at room temperature. The substrates were fully immersed in the suspension during 30 min so that the sedimentation of TiO₂ particles could occur. After that, the beaker was placed in a black chamber in order to prevent any contamination. The beaker was then placed in an oven (from memmert) at a temperature value of 85 °C during 30 min. After this temperature stage, the ceramic substrates were cooled down at room temperature in the same black chamber. The ceramic samples were removed from the TiO₂ suspension and dried in the same oven at a temperature value of 150 °C during 5 min to finish the resin curing process. At the end of the whole process, substrates were rinsed again with distilled water and dried at room temperature. A thickness of about 5.5 μm of TiO₂-NNPs based layer was obtained using this protocol.

Characterization of the TiO₂-NNPs coated ceramic surfaces

X-ray diffraction (XRD) analyses were carried out in order to evaluate the crystalline structure of both TiO₂ powder and TiO₂-NNPs based layers, deposited onto ceramic substrate. XRD 2θ scans were recorded by using a CuK_α radiation source in a *Philips PW 1710 X-ray Diffractometer*. Specific software was used to measure the precise 2θ positions and the full width at half peak maxima (WHPM) of the diffraction peaks. The crystalline grain size was calculated from the XRD pattern according to the Scherrer equation [27].

$$D_{hkl} = 0.94 \lambda / B_{hkl} \cos \theta \quad (1)$$

where D_{hkl} is the mean grain size with crystalline planes (hkl), B_{hkl} is the WHPM intensity in radians, and λ is the wavelength of the CuK_α radiation source.

The surface morphology of the produced TiO₂-NNPs based layers was observed by scanning electron microscopy (SEM) in a Leica Cambridge S360 instrument and by atomic force microscopy (AFM) from Digital Instruments controlled by Nanoscope III software. The optical reflectance and transmission spectra were recorded with a UV-visible scanning spectrophotometer, Shimadzu UV 3101 PC, in the spectral wavelength range from 300 nm to 700 nm.

In order to study the photocatalytic performance of TiO₂-NNPs based layers, a Methylene blue aqueous solution blue (C₁₆H₁₈N₃SCl) was prepared with an initial concentration of 0.5 mg/L. Methylene Blue dye is a heterocyclic aromatic chemical compound which has been widely used for photodegradation studies since it is an oxidation-reduction indicator. The TiO₂-NNPs coated ceramic samples were immersed in this solution in an open-top beaker with the irradiation perpendicular to the samples surface. UV lamps with a power of 12 W/m² (measured with Quantum Photo Radiometer HD9021 Delta Padova equipment) were used as the source of ultraviolet light and were positioned 30 cm from the beaker. After the irradiation experiments, performed for specific periods of time (namely 15, 30, 60, 120 and 240 minutes), a MB solution aliquot of 10 ml was placed in an open-top quartz cell, and the solution concentration was monitored by recording the transmittance spectrum using a Shimadzu 3101 PC spectrophotometer.

3. Results and discussion

The results obtained and their discussions are as follows.

Structural characterization

The crystalline phases of TiO₂ nanoparticles were evaluated by XRD (X-ray diffraction) and the obtained results are shown in Fig. 1.

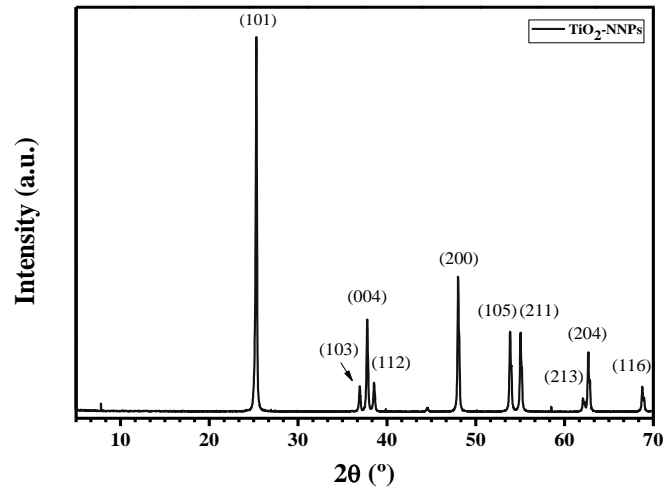


Fig.1. XRD diffraction patterns of TiO₂ nano-powder.

As shown in the diffractogram, the TiO₂ nanoparticles present evident diffraction peaks characteristic of the anatase phase. The polycrystalline anatase structure is mainly confirmed by the presence of (101), (004) and (200) diffraction peaks. Based on FWHM of (101) plane diffraction peak ($2\theta = 25.29^\circ$) the average crystalline size of TiO₂ nanoparticles was determined to be about of 30nm. XRD analyses were also performed in order to evaluate the crystalline structure of TiO₂-NNPs coated ceramic samples. In Fig. 2 are presented the obtained diffraction patterns for NP-G and NP-W ceramic substrates coated with TiO₂-NNPs based layers.

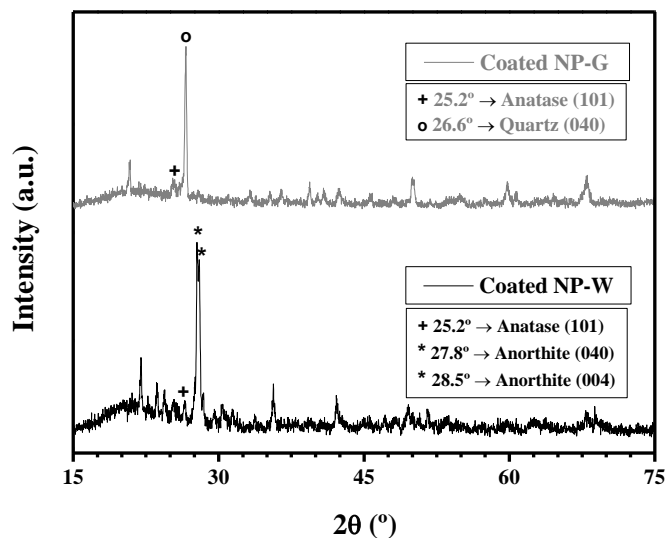


Fig.2. XRD diffraction patterns of TiO₂-NNPs based layers deposited onto NP-G and NP-W ceramics samples

It is possible to observe the appearance of new crystalline phases, which results from the substrate's material contribution. For example, in the NP-G sample it can be highlighted the presence of quartz, whereas for the NP-W sample, anorthite corresponds to the most intense peak. Nevertheless, the ceramic surfaces coated with the TiO_2 -NNPs based layers also present traces of (101) anatase diffraction peaks. We believe that the "apparent" decrease of the anatase intensity peaks, results from the huge thickness differences between the substrate material and the TiO_2 -NNPs based layer.

Surface characterization

The porosity and the roughness of the bare ceramic substrates have high influence not only in the adhesion between the TiO_2 -NNPs based layers and the ceramic surfaces, but also in their self-cleaning and photocatalytic performance [28,29]. SEM evaluated the surface morphology of the bare ceramic substrates and the TiO_2 -NNPs coated substrates in order to infer how TiO_2 nanoparticles are dispersed on the ceramic surfaces. Fig. 3 shows a SEM micrograph of the uncoated and TiO_2 -NNPs coated ceramic surfaces.

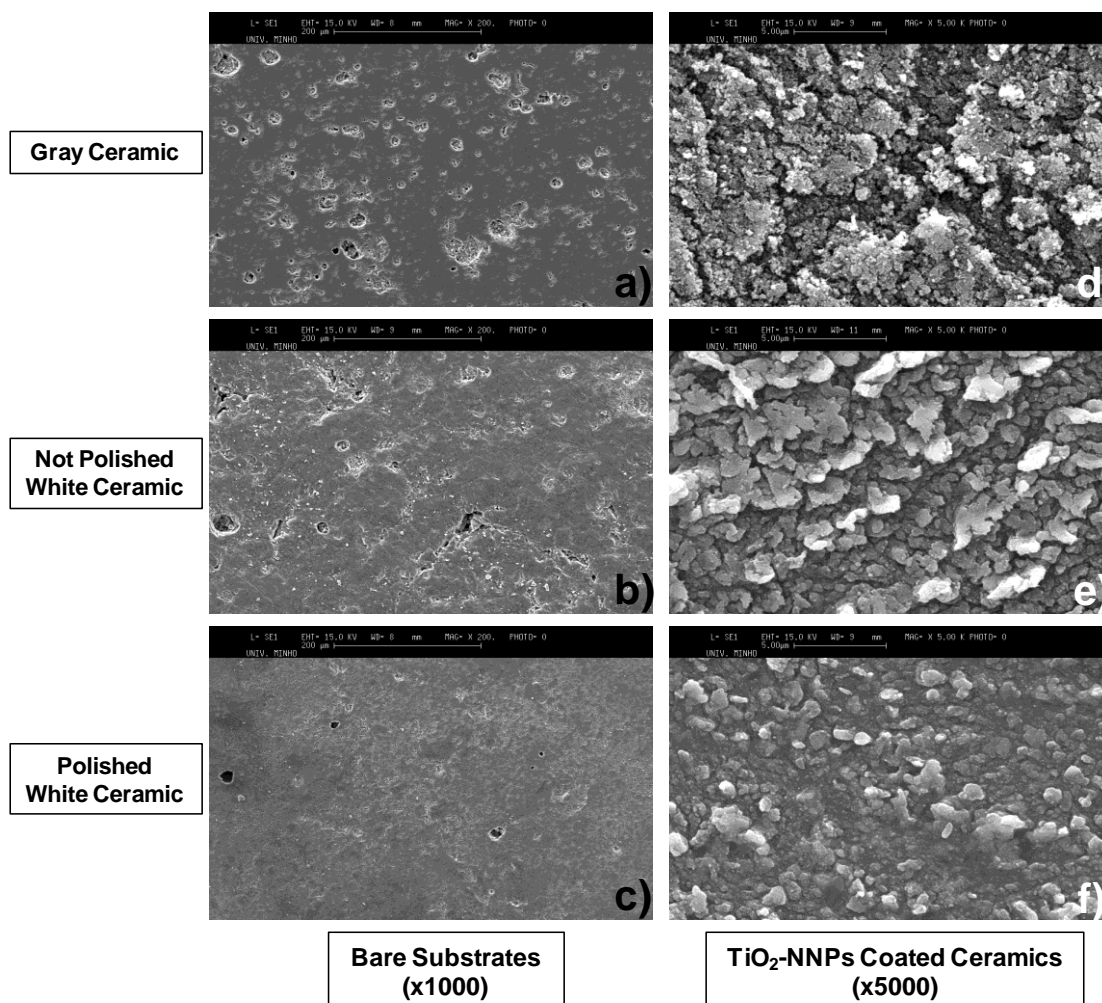


Fig.3. SEM micrographs of: (a)-(c) bare substrates; (d)-(f) TiO_2 -NNPs coated ceramics substrates

The surface finishing of the bare ceramic substrates is quite dissimilar. As it can be inferred from Fig. 3(a), NP-G ceramic substrate presents a huge amount of surface defects with large pores. In the case of the NP-W, Fig. 3(b) shows that for this sample the surface finishing is a bit better but still has some surface defects. As expected, the P-W ceramic substrate presents the highest surface quality (Fig. 3(c)).

Regarding the ceramic samples coated with the TiO₂-NNPs based layers, it can be observed that all of them present a highly pored surface structure in which the TiO₂ nanoparticles tend to aggregate, forming clusters. However, some differences can be highlighted: for example, the coated NP-G ceramic sample shows the most heterogeneous TiO₂ nanoparticles agglomeration (Fig. 3(d)) whereas in the case of the P-W ceramic sample, the particles agglomerations are more homogeneous and exhibit clusters with smaller sizes (Fig. 3(f)).

In order to evaluate the dispersion way and the average roughness of the TiO₂-NNPs based layers, an additional flat glass sample was prepared, using the same experimental protocol. Fig. 4 is shows a 3D AFM surface image of a TiO₂-NNPs based layer, deposited on the surface of a glass substrate.

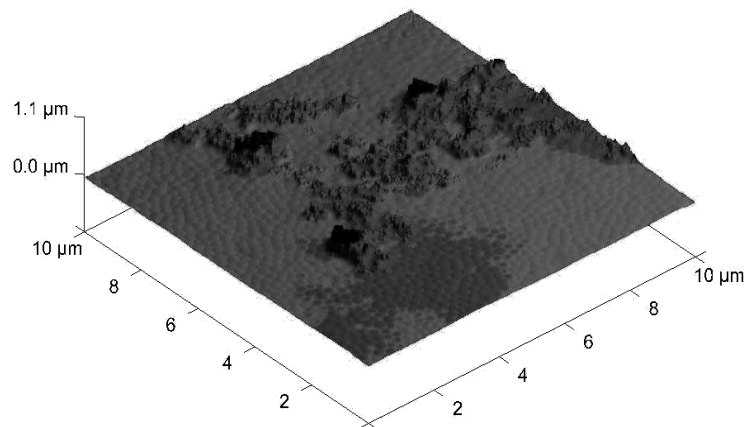


Fig.4. AFM image of a TiO₂-NNPs coated glass surface, prepared by the dip-coating method

The TiO₂-NNPs coated glass surface reveals a certain degree of roughness ($R_a \sim 33.8\text{nm}$). In addition, it can be also identified the presence of some heterogeneous particles agglomeration imbibed in regions with high structural densification.

One of the major concerns in this work is the development of ceramic surfaces with self-cleaning and photocatalytic ability, without damaging their aesthetical feature. In order to monitor the changes on the aesthetical characteristics (eventually promoted by the TiO₂-NNPs based layers) of the coated ceramic surfaces, optical reflectance spectra were used as quality control tool. The reflectance spectra of the bare ceramic samples and the TiO₂-NNPs coated substrates are shown in Fig. 5.

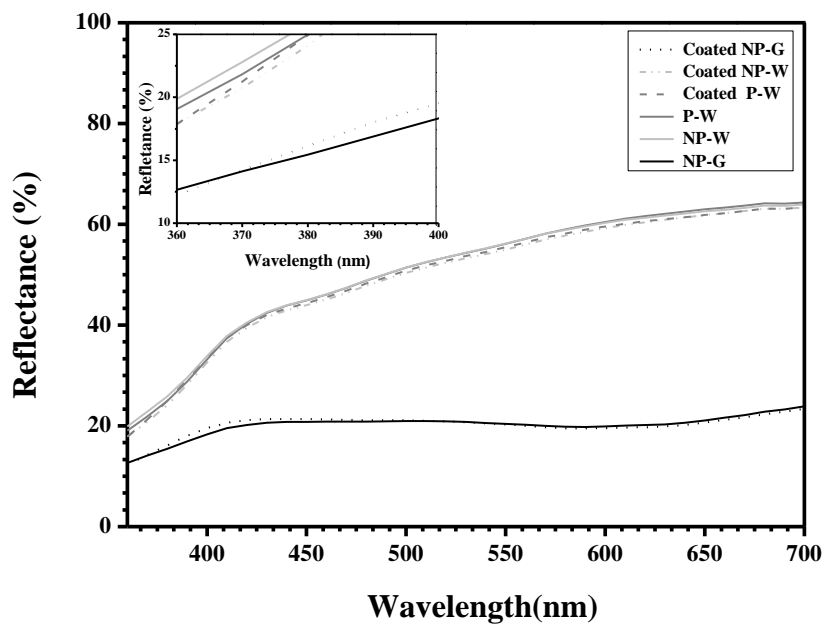


Fig.5. Optical reflectance spectra of bare and TiO₂-NNPs coated ceramic surfaces.

As expected, nevertheless the kind of the material burnishing, white ceramics samples present the highest value of optical reflectance in the visible region of electromagnetic spectrum. Furthermore, it can be observed that for the all TiO₂-NNPs coated samples, the optical reflectance did not change. Thus, it can be concluded that the surface aesthetical appearance has been maintained.

Photocatalytic activity

The photocatalytic behaviour of the TiO₂-NNPs based layers was assessed by combined ultraviolet irradiation and transmittance measurements. Fig. 6 shows the increase in transmittance of the MB aqueous solution after irradiation and photocatalytic action by the coated NP-G ceramic sample. The observed photodecomposition of the aqueous solution (organic pollutant) can be seen in the UV/Vis spectrum by the increase of the minimum transmittance (monitored at 664 nm) with irradiation time.

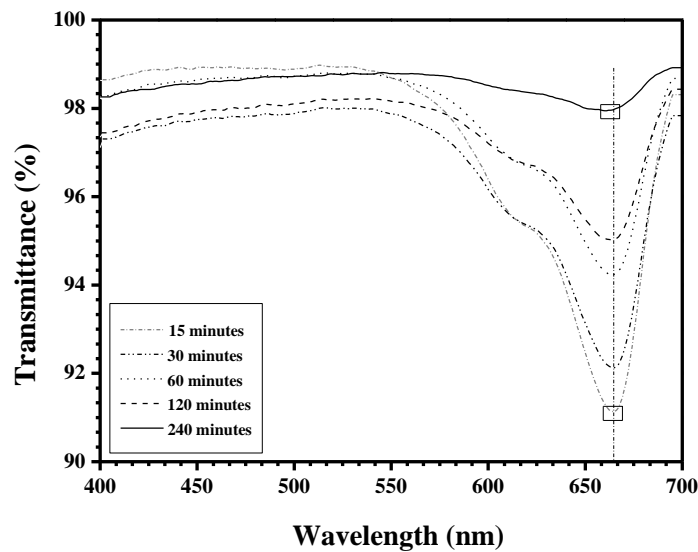


Fig.6. Transmittance spectra of MB aqueous solution taken at five times during irradiation and under the photocatalytic action of TiO_2 -NNPs based layers.

The colour of the dye changes from bright blue to colorless during this process, hence indicating that the chemical oxidation-reduction mechanisms are taking place on the surface of the TiO_2 NNPs coated ceramic sample. It should be noted that, under similar UV irradiation conditions, the absence of a photocatalyst material did not affect the dye's concentration. From the transmission data it is possible to obtain the decrease in the solution concentration as a function of UV irradiation time.

At low concentrations, the Beer–Lambert law dictates that the transmittance, T , is related to the solution concentration through the following equation:

$$\ln T = -\epsilon l c \quad (2)$$

where ϵ is the molar extinction coefficient, l the optical path length, and c is the concentration of the absorbing compound in the solution. Since the two parameters ϵ and l are constant, then:

$$\frac{\ln T}{\ln T_0} = \frac{c}{c_0} \quad (3)$$

where the subscript 0 is related to time zero ($t = 0$). The rate constant for this process, k , can be calculated by means of a pseudo-first-order reaction [30]:

$$\ln \frac{c}{c_0} = -k t \quad (4)$$

The photocatalytic activities of the TiO₂ NNPs coated ceramic samples can be compared by using *k* values, calculated from the slopes of the fitting lines represented in Fig. 7.

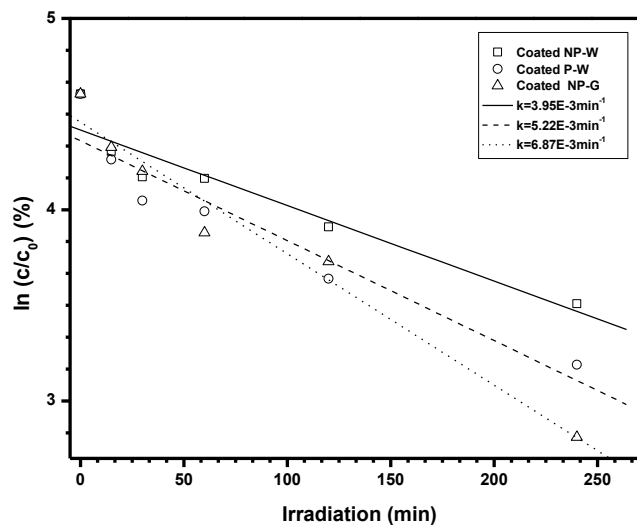


Fig.7. Photodegradation of the MB aqueous solution under the irradiation of UV light.

From the experimental data in Fig. 7, it is observed that the coated NP-G sample shows the highest photoactivity; this sample, presents the highest photodegradation rate constant ($\sim 6.9 \times 10^{-3} \text{ min}^{-1}$). Possible explanations could be based on the fact that this coated sample has a rougher TiO₂ nanoparticles aggregation with a highly pored surface. In this case, MB aqueous solution can intrude the pores, and then being easier absorbed into deeper levels of the deposited TiO₂ layer in order to participate in chemical redox reactions. Meanwhile, the coated P-W sample, which contained the lowest surface porosity, did not show a particularly high decrease ($\sim 24\%$) of the rate constant with respect to the coated NP-G sample. We believe that the reason why this phenomenon is occurring is related with another kind of competitive contribution. For the coated P-W sample, the TiO₂ nanoparticles agglomerations are more homogeneous and exhibit clusters with smaller sizes (see Fig. 3(f)); therefore, as the grain size of these clusters is decreased, the surface-to-volume ratio is increased and the photo-generated electrons and holes could undergo a short pathway to migrate to the surface. Thus, the (e^-/h^+) volume recombination rate should decrease, giving rise to an improvement in photocatalytic activity. The analysis of the transmittance data also allows us to obtain the photocatalytic efficiency (η %) according with the following equation:

$$\eta(\%) = \left(1 - \frac{\ln T}{\ln T_0} \right) \times 100 \quad (5)$$

where T is the solution transmittance at $t = 240$ min and the subscript 0 is related to time zero ($t = 0$). From Eq. (5) the calculated photocatalytic efficiencies of the coated NP-G, P-W and NP-W samples, are respectively 83%, 76% and 67%.

Wettability (self-cleaning) properties

Surface wettability was evaluated via contact angle measurements in a dynamic mode using Young La Place method (Contact Angle System S.A data physics) with $5\mu\text{l/s}$ of distilled water droplets. Contact angle (CA) formed by water on samples surfaces was measured in order to assess how samples wettability changed after UV irradiation. Fig. 8 (a) is an image that shows the changes in CA that have been obtained (after UV light irradiation) for the coated NP-G ceramic sample, and Fig. 8 (b) presents for all the coated samples the percentage variation (decrease) of CA, referred to their initial value.

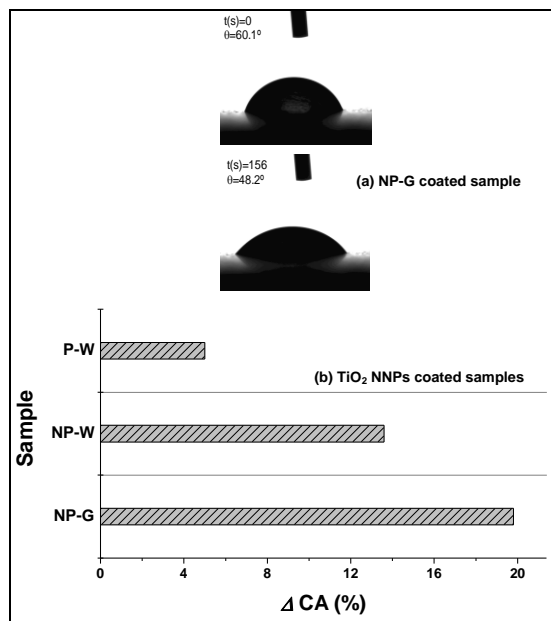


Fig.7. (a) Changes in the water CA and (b) percent decrease of CA of water on the tested samples.

All tested samples have hydrophilic surfaces and thus they allow the surface to be more easily cleaned by rain (self-cleaning effect). In addition, after UV irradiation they show a slightly decrease of CA value: in any case, once more the best result (most hydrophilic) was obtained with the coated NP-G sample which shows the higher percentage decrease of the CA value, and also present the highest photocatalytic efficiency. Nevertheless the coated P-W sample presents moderate photocatalytic efficiency it didn't show a moderate decrease of CA values after UV irradiation. However, these results indicate that porosity and roughness affects the surface wettability.

4. Conclusions

Colorless TiO_2 -NNPs based layers were successfully deposited onto gray and white ceramic substrates, using the dip-coating method without changing their aesthetical look. Prior to TiO_2 nanoparticles deposition, both the precursor powders and the substrates were characterized so that their influence could be analyzed. All the produced TiO_2 -NNPs based layers showed the anatase crystal phase, however the highest photocatalytic performance was achieved for the coated gray ceramics; a photodegradation rate of $6.9 \times 10^{-3} \text{ min}^{-1}$ and a photocatalytic efficiency of 83% was found. The mentioned coated sample allowed the attainment of a moderate self-cleaning ability and a noticeable photodegradation capacity. The obtained results were discussed taking into account the different surface morphologies of the produced surfaces: the surface wettability of TiO_2 -NNPs coated ceramic materials are influenced by porosity and roughness.

With this work it is believed that in a near future, an interesting solution may be presented aiming the reduction of high maintenance costs related with the preservation of building pavements and facades. At the same time environmental quality can be improved by reducing the use of toxic reagents for cleaning.

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