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(Article begins on next page)

Photocatalytic Porcelain Grés Large Slabs digitally coated with AgNPs-TiO_2

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Abstract

TiO_2 is employed as both photocatalytic and structural materials, leading to its applications in external coatings or in interior furnishing devices, including cement mortar, tiles, floorings and glass supports. The authors have already demonstrated the efficiency of photoactive micro-sized TiO_2 and here its industrial use is reported using the digital printing to coat porcelain grés slabs. Many advantages are immediately evident, namely rapid and precise deposition, no waste of raw materials, thus positively affecting the economy of the process. Data for the thin films deposited by digital printing were compared with those obtained for the conventional spray method. The use of metal-doped TiO_2 is also reported so that the photoactivity of these materials can be exploited even under LED light. The digital inkjet printed coatings exhibited superior photocatalytic performance owing to both higher exposed surface area and greater volume of deposited anatase, as well as the greater areal distribution density of thinly and thickly coated regions. Moreover, the presence of TiO_2 doped silver increased the efficiency of the materials in NOx degradation both under UVA and LED lights.

Keywords:

Micro-sized TiO_2; photocatalysis; building materials; porcelain grés materials; Ag-doping; digital printing; LED light; NOx

1. Introduction

Concern for the impact of air quality on human health has been increasing for many decades (Fullerton 2008, Kurmi 2010). A 2014 World Health Organization (WHO) health report (WHO

2014) states that there were about 7 million deaths globally from air pollution, 60% of which due to indoor pollution, 53% were from outdoor pollution, and the overlap of 14% was from a combination of the two. Furthermore, the effects of air pollution on the welfare and survival of native flora and fauna remain topical issues. In general, air pollution can be addressed by the two different approaches of either prevention or elimination (Ren 2017). In the latter case, there is an imperative request to both develop new and improve existing techniques for the destruction of air pollutants.

Contrary to what is generally assumed, air in several indoor environments is often more polluted than outdoor, because of the many sources of indoor pollution, which include mold and pollen, tobacco smoke, household products and pesticides, and materials usually used in buildings such as formaldehyde and organic compounds in general. Health effects from indoor air pollutants generally occur after long or repeated exposure and they can be severely debilitating or fatal: moreover, mainly in the urban areas in more developed Countries, population spends most of the time in closed rooms, houses, offices and schools (80-90% of a day).

There is still uncertainty about the level of concentrations that can produce specific health problems. However, it is accepted that even low concentrations of some ubiquitous pollutants can be very dangerous, often causing undesired effects on health from sensory discomfort to serious consequences for physical conditions.

Photocatalysis is one of the most promising methods to purify air. For this reason, photocatalytic materials and technologies for air purification have emerged as some of the most intensively examined approaches to this end (Ren 2017, Zhao 2003, Mo 2009, Huang 2016, Chen 2009). Titania (TiO_2) is one of the most suitable semiconductor materials for such photocatalytic applications owing to its photocatalytic activity, chemical and environmental stabilities, nontoxicity, and economy. Among the three TiO_2 polymorphs (i.e., anatase, rutile, brookite), anatase is recognised as being the most effective photocatalyst (Hanaor 2011).

New class of building materials can be a good tool to play an active role in environment remediation. At the beginning of the industrial productions, porcelain grés tiles were considered as just a technical material, aesthetically not very beautiful. Today, thanks to new industrial production methods, both properties and appearance of these materials completely fit the market requests. In particular, the possibility to prepare slabs of large sizes is the new frontier of building materials.

However, it is time to go further the simple sustainable materials and to produce cements and tiles and in general building materials no longer inert but able to ”work” to improve the well-being of people living in those spaces. In fact, besides the noteworthy architectural features, new surface properties can be introduced in the last generation of eco-active materials. In particular, deposition of TiO_2 transforms the traditional ceramic surface into a photocatalytic eco-active material able to (i) reduce polluting molecules present in air and water, (ii) to eliminate bacteria and (iii) to reduce the surface dirt thanks to the self-cleaning property. The standard requirements of the porcelain grés with respect to hardness, lack of porosity, vitrified surface, durability typical of a porcelain grés product do not change with the addition of the photocatalytic coating.

The digital printing was exploited as a new tool to manufacture photocatalytic tiles even of very large size (150x300 cm). Conventional spray coating and dip coating methods are basic techniques, typically involving aqueous suspensions, applied to substrates over relatively large areas. In contrast, digital inkjet printing is more sophisticated, involving piezoelectric heads with precise directional deposition of an aqueous/organic suspension with an electrostatic field; details of the process are available elsewhere (Bianchi 2018). Micro-TiO_2 was industrially formulated in a tailored ink, digitally printed at the tiles surface, fired in industrial kiln at 680°C and cleaned with a rotating wire brush to remove the TiO_2 fraction weakly stuck at the ceramic surface. In the formulation, a commercial micro-TiO_2 (Kronos, characterized by pure anatase and a not coated surface) was employed avoiding the use of traditional nano-sized TiO_2 in powdery form, thus preventing possible side effects on human health due to both use and exposure to nanoparticles mainly during the manufacture process.

A frequent criticism to photocatalytic materials concerns their use only in the presence of sunlight or traditional artificial lamps, but not with the recent LED lights that have a type of radiation incompatible with the activation of traditional TiO_2. All the photocatalytic processes are inexorably turned off when the material is illuminated by LED lights and, even more so, when in darkness. For this reason, the commercial micro-sized TiO_2 was decorated with Ag nanoparticles (Ag-NPs) to enhance its activity even in the visible region (Cerrato 2019).

Seery and co-authors reported about Ag modified TiO_2 materials with increased visible light activity compared to bare TiO_2 (Seery 2007) due to the surface plasmon band of Ag, which absorbs in the visible spectrum (Nolan 2010). The scientific literature is rich of both procedures and data on the synthesis of Ag-NPs supported on TiO_2. Examples include impregnation from Ag colloidal dispersions (Yu 2017) or from Ag inorganic salts (Amruta 2016), electrostatic self-assembly (Li 2017), photo-reduction of Ag salts (Milosevic 2017), or ultrasound-assisted synthesis (Stucchi 2018).

The photocatalytic properties of commercial digitally coated slabs, photoactivated both with bare TiO_2 and AgNPs-TiO_2, were verified in laboratory using NOx as model pollutant, to evaluate the good performance of the ceramic slabs to tackle the environmental pollution both under UV and under a commercial LED lamp. The presence of the dopant metal allows the material to act also as antibacterial both in the UV or LED light and in the dark, by eliminating one of the negative features of photocatalytic building materials that has so far limited their use on a large scale.

2. Materials and methods

The support was a micrometric pure anatase TiO_2 (K1077, KRONOS Worldwide, Inc.), as assessed by its crystallographic structure: we thoroughly characterized it in previous works (Bianchi 2015) and its main features are here below summarized (Table 1).

Table 1. Characteristics of Kronos 1077 TiO_2 Powder

Characteristic	**Units**	**Value**
Mineralogy	wt%	≥98.5 Anatase
pH	--	7.0 – 8.5
Brightness	--	97.0 – 97.8
True Density	kg/m^3	3800
Particle Size Range	nm	110 – 130
Surface Area	$m^2 \cdot g^{-1}$	12
Optical Indirect Band Gap	eV	3.15
Band gap	eV	3.15
XPS (OH/O_{TOT})		0.32

2.1 AgNPs and AgNPs-TiO_2 preparation

AgNps-doped TiO_2 was prepared following two different synthetic procedures. The first one implied to start from silver nitrate ($AgNO_3$, ACS Reagent, ≥99%). The other reagents were polyvinylpyrrolidone (PVP40, average mol wt 40,000) and ammonia (NH_3, ≥99%). The preparation of the AgNPs sol is reported elsewhere (Minozzi 2018). The second preparation was carried out starting from a commercial AgNPs solution (Fluka).

In both cases, the final product was obtained by simple wet-impregnation of the AgNPs sol with the microsized TiO_2 K1077 for 24 h at room temperature and final calcination at 450°C for 2 h.

2.2 Industrial ceramic tiles production

Tiles under investigation were commercial porcelain grès large slabs, manufactured by IrisCeramica Group. Industrial porcelain-grès tiles are produced under high pressure by dry-pressing finely processed ceramic raw materials with large proportions of quartz, feldspar, and other fluxes and finally fired at high temperatures (1200– 1300 °C) in a kiln. Commercial photoactive porcelain-grès tiles were subsequently covered at the surface with a mixture of either pure TiO_2 (product label: digital Active) or TiO_2 doped with AgNps (product label: Active 2.0), mixed with a tailored SiO_2-based ink by digital printing (Projecta Engineering, Italy) (Bianchi 2018). To ensure the requested product stability, at the end of the preparation procedure, the tiles were treated at high temperature (680 °C) for 80 min and then brushed to remove the powder present at the sample surface and not completely stuck. The temperature was precisely chosen to maintain the anatase form of the semiconductor and allow the vitrification of the tile surface (Bianchi 2018).

2.3 Sample Characterization

Micro-sized powders were characterized by Transmission Electron Microscopy (TEM). Images (either conventional or in high resolution) have been obtained by means a Jeol JEM 3010 UHR instrument, equipped with a LaB_6 filament (operating at 300 kV) and an Oxford INCA X-ray energy dispersive spectrometer (X-EDS) with a Pentafet Si(Li) detector. Samples were “dry” dispersed on lacey carbon Cu grids.

Furthermore, tiles were characterized by SEM and EDX analyses, using a Field Emission Gun Electron Scanning Microscopy LEO 1525, metallization with Cr. Elemental composition was determined using Bruker Quantax EDS.

2.4 Photocatalytic tests

The photocatalytic activity of the samples was tested for NOx degradation. Their efficiency was monitored using a setup precisely described elsewhere (Ardizzone 2007) operating in static condition. Photocatalytic degradations were conducted in a Pyrex glass cylindrical reactor with an effective volume of 20 L. The gaseous mixture in the reactor was obtained by mixing NO_2 (0.6% in nitrogen) with air humidified at 40%. It is important to underline that we start from an inlet gas of pure NO_2 pulsed into the reactor that, as soon as it comes into contact in the air already present, reaches the chemical equilibrium between NO and NO_2. In this way all the photocatalytic tests have been made using a mixture of NO and NO_2 in air. Two initial concentrations of NOx in the reactor were tested: 1000 ppb in order to follow the same pollutant concentration requested by the ISO 22197-1:2016 rules (ISO 2016) and 500 ppb for the tests performed under LED light.

Photon sources were provided by a 500W iron halogenide lamp (Jelosil, model HG 500) emitting in the 320–400 nm wavelength range (UV-A) with a specific UV power on the surface of the samples of 20Wm^{-2}and by a commercial LED lamp (Philips) emitting >420 nm wavelength irradiating 1000 lux. In all cases, UV and LED lights emissions were measured using a photo radiometer (Delta Ohm – HD2101.2 model).

NOx photocatalytic tests were performed at 25°C for 6 h. The actual concentration of pollutants (NO, NO_2 and consequently their sum, i.e. NOx) in the reactor was determined directly by chemiluminescence (Teledyne, Mod. 200E).

3. Results and discussion

Conventional and HR-TEM images of the various samples have been obtained and the relevant results are summarised in Figure 1.

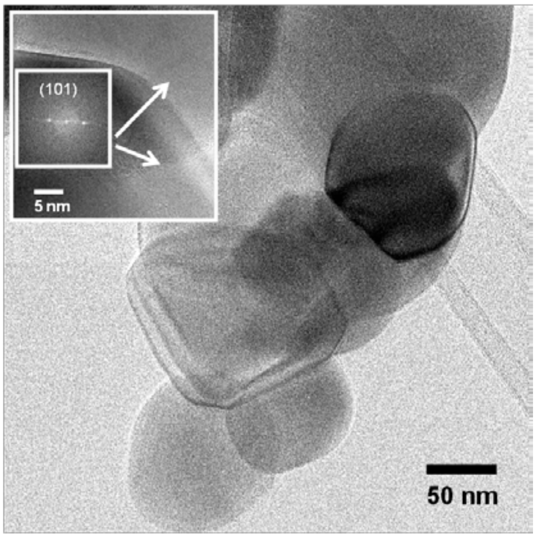

Figure 1a. TEM images of the plain micrometric TiO_2.

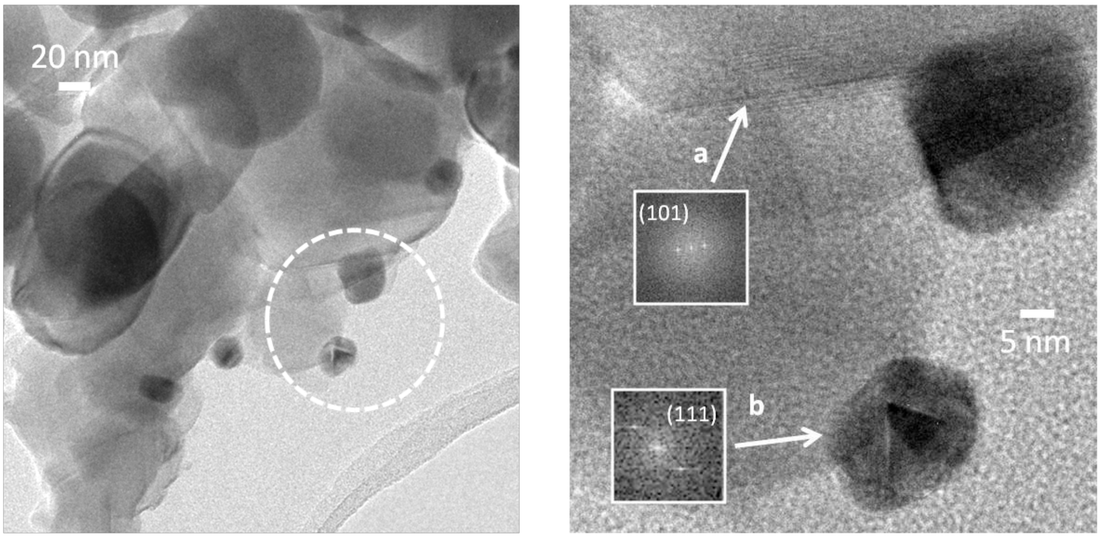

Figure 1b. TEM images of AgNPs-doped TiO_2. Left-hand section: low magnification image. Right-hand image: high magnification image and electron diffraction patterns.

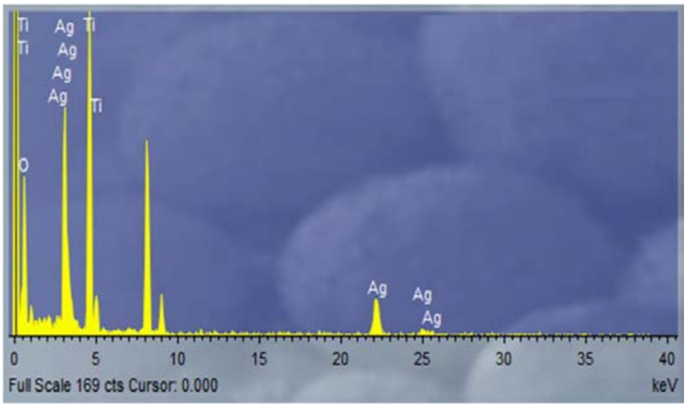

Figure 1c. EDS spectrum relative to the left-hand image reported in figure 1b

The morphological features of plain micrometric TiO_2 remains unchanged after the addition of Ag species as it can be observed in Figure 1a. Both at low magnification (main image) and at high magnification (inset to Figure 1a), large and ordered micro-crystals are evident, almost all exhibiting smooth edges and a 100-130 nm average size dimension. The inspection of the fringe patterns indicated by the arrows (and of the relevant electron diffraction) indicates that the family of planes most frequently exposed is the (101) of the TiO_2 anatase phase [ICDD 21-1272]. As for the samples containing Ag species (see Figure 1b), no morphological peculiarities could be singled out for what concerns the TiO_2 support, indicating that the addition of Ag brings about no changes on it. On the other hand, the presence of Ag species is well assessed by (i) the EDS spectrum reported in the left-hand image of Figure 1b, and (ii) also by the inspection of the fringe patterns/electron diffraction marked with b (see the right-hand image): the crystal planes put into evidence are those related to the (111) family of metallic Ag [ICDD 01-0783] and the average dimensions of these metal particles resides in the nanometric range, being located in the 10-20 nm.

The particles distribution on the ceramic surface was evaluated by SEM analysis. Fig.2 reports that, by means of the digital printing process, it has been possible to disperse in a uniform waythe micro-sized particles of the photocatalyst at the surface of the tiles, thank for the ink containing the TiO_2 powder (K1077) and delivered by the printing heads.

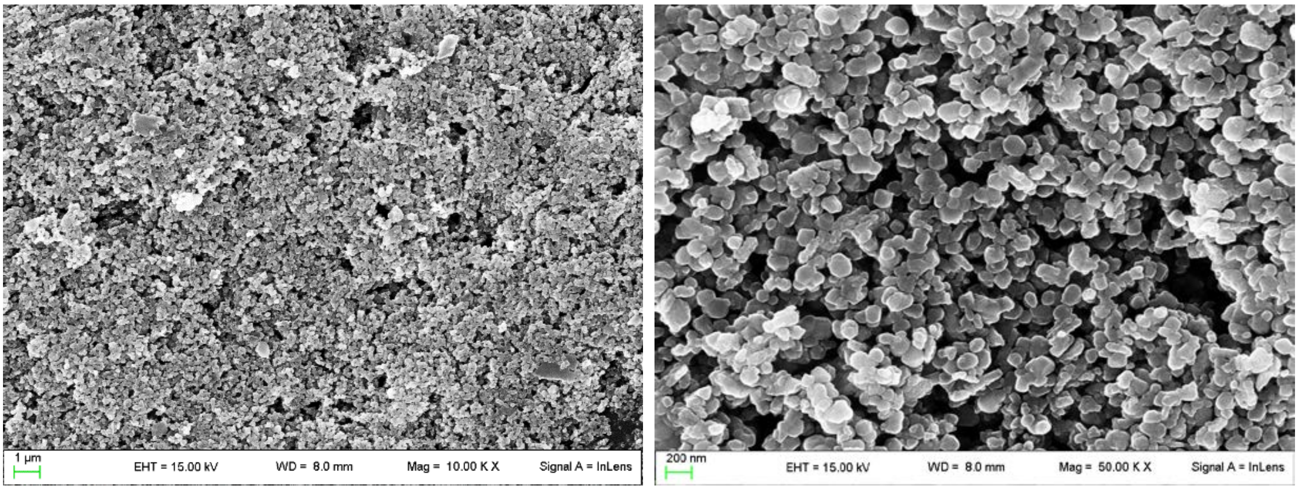

Figure 2 - SEM images of AgNPs-doped TiO_2 coated on the ceramic surface obtained after digital printing process. Left-hand section: low magnification image (10 KX). Right-hand image: high magnification (50 KX).

The single element distribution can be appreciated by EDX characterization carried out bduring the SEM analysis (Fig.3). Both Ag and Ti are homogeneously dispersed on the tiles surface with some small voids in the Ti presence due to the peculiar tile texture. In fact, the black spots are raised areas of tile structure where TiO_2 has been partially removed by the industrial brushing process carried out downstream to the production and aimed at the removal of the excess photocatalyst powder not perfectly adhered to the ceramic surface. The average amount of TiO_2 coated on the tile surface as 20 g m^{-2} as fixed by the digital printer and confirmed by EDS measurements.

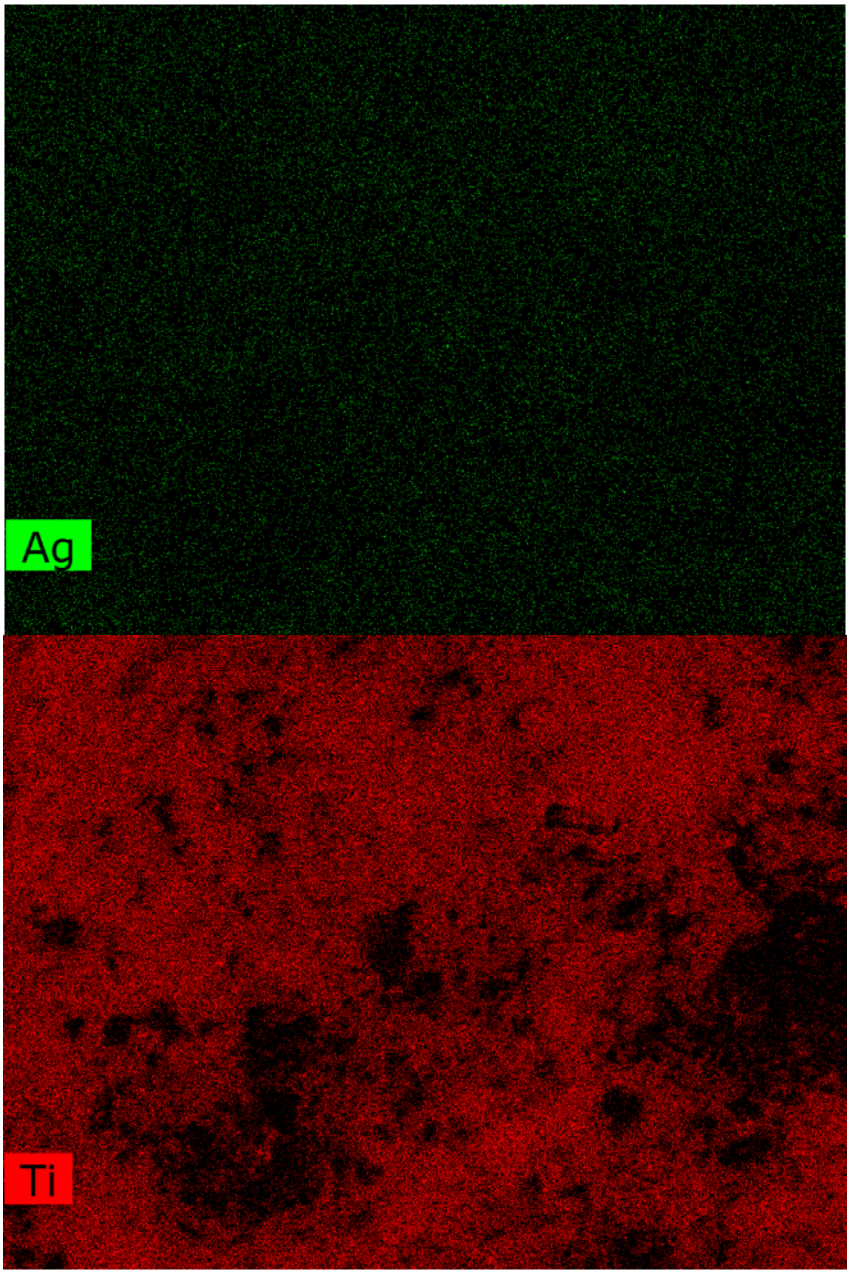

Figure 3 - EDX images of AgNPs-doped micro-sized TiO_2 coated on the ceramic surface obtained after digital printing process. 1) Ag distribution: green spots 2) Ti distribution: red spots

The characterisation results obtained so far in terms of uniformity of the photocatalyst on the surface allow us to predict that the activity towards the NOx degradation of the ceramic slabs produced with the digital technology (digital Active) can be considerably higher than that obtained with the tiles produced with the old spray technology (spray Active). In addition, the new slabs produced with the K1077 doped with AgNPs (Active 2.0) show, as foreseen by the tests on the photocatalyst in powdery form (Bianchi CL 2018a) that the Ag brings about a beneficial effect in terms of greater efficiency of the ceramic as anti-pollutant material under UVA lights (Fig.4).

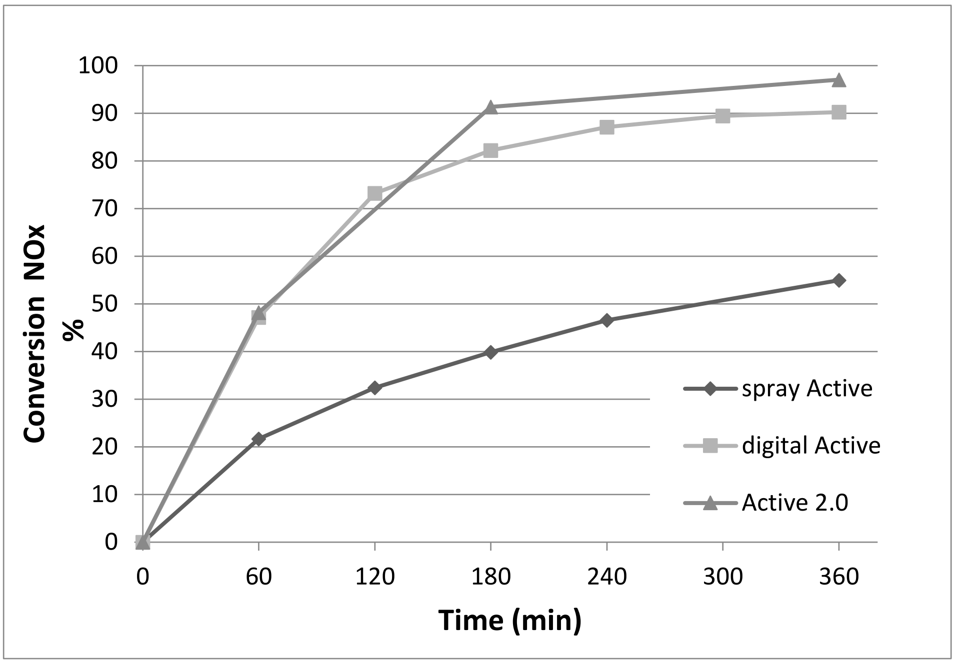

Figure 4 – NOx (1000 ppb) conversion vs time. Tests performed on industrially produces ceramic tiles using: ▲ AgNPs-K1077 digitally printed (Active 2.0); ■ K1077 digitally printed (digital Active); ♦ K1077 coated by spray on the ceramic surface (spray Active).

It is possible to observe that the NOx photoabatement greatly increased from 56 to 90% on passing from spraying technology to digital printing, indicating that the latter allowed a greater uniformity in the surface distribution of the photocatalyst. The presence of the decoration with AgNPs on the K1077 has even more increased the effectiveness of ceramic material up to 96% NOx conversion with UVA lamp.

The general mechanism of NOx oxidation by photocatalysis implies their oxidation to either nitric or nitrous acids by active oxygen species produced on the TiO_2 surface. In particular, in a previous work we investigated the NOx photodegradation with micrometric TiO_2 using a 60x60 cm tiles activated with TiO_2 (Bianchi 2016). As expected, the reaction follows a pseudo first order respect to both NO and NO_2 to form oxidized species (i.e., NO_3^-).

The major challenge for photocatalytic construction materials lies in their activity even in visible light, and even more so under LED lights where UVA radiation is zero, light source increasingly used both indoors and outdoors for reasons of energy saving.

Tests carried out on the K1077 powders doped with AgNPs demonstrated the efficacy of the photocatalyst even under LED lights and, for this reason, specific tests were carried out with the same type of light source at 1000 lux also on ceramic tiles (see Table 2). No photoactivity was obtained for the old technology via spray coating, but this is also negligible even via digital printing using the commercial TiO_2. On the contrary, it is possible to observe a good NOx degradation even in the absence of UVA irradiation for the ceramic surface coated with K1077 doped with AgNPs, confirming the results obtained with the photocatalyst in powder form (Cerrato 2019).

Visible light is insufficient to excite electrons from the valence band to the conduction band. Photodegradation under LED as the only source of light is impossible with naked TiO_2 because of its wide band gap of 3.2 eV. Ag nanoparticles absorb visible light due to the plasmonic resonance; moreover, by settling on the TiO_2 surface they create a junction permitting the electron transfer from Ag to TiO_2 and the number of electrons available at the surfaces increases. Consequently, the concentration of photo-generated species at the TiO_2 surfaces is higher and the oxidation and reduction more likely to occur (Stucchi, 2018).

Sample	**NOx degradation under LED light (%)**
Ceramic tile sprayed coated with K1077	0%
Ceramic slab digitally printed with K1077	10%
Ceramic slab digitally printed with AgNPs-K1077	46%

Table 2 – NOx degradation (500 ppb) under LED light after 6 h

4. Conclusions

The digital inkjet printed coatings employed in the present research activity has been demonstrated to possess superior photocatalytic performance owing to both higher exposed surface area and greater volume of deposited anatase, as well as a greater areal distribution density of thinly and thickly coated regions. Moreover, the presence of Ag-NPs has been found to greatly increase the efficiency of the materials in NOx degradation both under UVA and LED lights: this aspect has been thoroughly investigated also in the case of large ceramic slabs, prepared with the same digital printing technology, leading to very interesting results opening the door for antipollution applications in real environment.

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