PHOTOCATALYTIC NANOSTRUCTURED TiO_2 FOR PROTECTION OF POROUS AND COMPACT STONE

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Abstract

The enhanced photocatalytic activity for degradation of a wide range of pollutants makes nanostructured TiO_2 an ideal candidate for self-cleaning coatings.

The deposition of different types of TiO_2 nanocrystalline coatings on stone has been investigated in order to test the surface protection and self-cleaning abilities of the nanostructured materials. TiO_2 nanocrystals with controlled size, shape and surface chemistry have been prepared by using two distinct synthetic approaches, namely colloidal synthesis by hot injection and hydrothermal nanophase crystallisation. Two different types of stones, possessing different porosity, namely porous calcarenite and a compact limestone have been selected, being both widely used in South Italian monuments and building relevant for cultural heritage.

The physical properties of coated and uncoated stone surfaces, respectively, have been investigated, and colour, wettability and stability of the coatings have been checked. The self-cleaning properties of the nanostructured TiO_2 coated surfaces under solar irradiation have been tested by monitoring the degradation of a model organic molecule, namely an organic dye. The obtained results have confirmed that the nanocrystalline TiO_2 coatings are promising candidate for environmental protection upon appliance on either porous and compact stone. Moreover, the nanostructured TiO_2 obtained colloidal synthesis by hot injection has demonstrated to provide hydrophobic treated surfaces.

Keywords: TiO_2 nanocrystals, hydrophilic and hydrophobic treatments, calcareous stones, cultural heritage.

1. Introduction

TiO_2 is generally recognized as one of the most interesting compounds in several technological fields based on photoinduced phenomena (Chen, et al.,2007). In particular, many efforts have been devoted to the environmental applications of TiO_2, due to its efficiency in photocatalytic degradation of both organic and inorganic compounds. Indeed TiO_2 is regarded as one of the most efficient, non-toxic, and inexpensive photocatalysts (Carp, et al.,2004). When TiO_2 is irradiated with photons with energy higher than or equal to its band gap energy, electrons (e^-) and photo-holes (h^+) are created (Herrmann,2010). These charges can migrate to the surface and react with adsorbed electrons donors or acceptors. In this step strongly reactive radicals, potentially able to mineralize a target molecule, are generated (Herrmann,1999).

In the last decade growing attention has been devoted to the exploitation of nanosized semiconductors in photocatalysis. Indeed nanostructured catalysts show higher photocatalytic activity than their bulk counterpart, as they are characterized by high surface to volume ratio thus resulting in higher density of active sites for adsorption and catalysis (Comparelli, et al.,2005)

Nanostructured photocatalytic materials have been exploited in several technological fields, including air cleaning, water purification (Teoh, et al.,2012), and bacteria inactivation (Rengifo-Herrera, et al.,2009) as well as in the construction industry, to keep supplementary functions to windows glass, pavement, walls and roofs. (Lee, et al.,2010)

A challenging task is represented by the possibility of exploiting TiO_2 nanoparticles for protection and conservation of cultural heritage, in order to prevent pollution and darkening of monuments and buildings. In particular, the opportunity of coating surface of stones with photoactive TiO_2 nanoparticles could grant self-cleaning properties to the treated surfaces (La Russa, et al.,2012, Quagliarini, et al.,2012). Nonetheless, the application of coating for such a kind of treatment presents some fundamental requirements, as chromatic change of the treated materials, their water absorption ability by capillarity, and their permeability (Licciulli, et al.,2011). Herein, TiO_2 nanocrystals have been prepared by exploiting two distinct synthetic approaches namely, hydrothermal crystallization and colloidal synthesis by hot-injection, which provides nanocrystals with a rod-like geometry, and deposited on two different lithotypes, characteristic of the South of Italy, namely “Pietra Leccese” (PL) and “Pietra di Trani” (PT) as distinct examples of porous calcarenitic stone and compact limestone, respectively. The morphological, physical and photocatalytic properties of the coating have been investigated by colorimetry and reflectance spectra. The photocatalytic properties of the coating have been tested in the degradation of a model compound (an azo dye, Methyl Red) under solar irradiation. The obtained results suggest that both nanocrystalline TiO_2 based coatings seem good candidates for environmental protection of stone materials. In addition, TiO_2 nanorods prepared by hot-injection technique could confer hydrophobic properties to the stone.

2. Experimental section

2.1 Synthesis of hydrothermal TiO_2 nanocrystals

An aqueous colloidal suspension, of hydrothermal TiO_2, has been prepared using tetrapropyl orthotitanate (TPOT) from Sigma-Aldrich 97% as TiO_2 precursor.

First, 5.7 g Hydrate oxalic acid (Carlo Erba 99.8%) have been dissolved in 957.6 g of deionised water, then 37 g of TPOT have been added dropwise.

The precipitate has been readily dissolved by stirring and heating in about 2 h until a TiO_2 amorphous sol has been obtained. After that the sol has been processes in Teflon-lined autoclave (Mars 5, CEM Corporation) for different dwells at the temperature of 125 °C and at the pressure of 3.5 bar. The heating rate was 2.5 °C/min. The temperature was maintained with the accuracy of ±2 °C. The maximum process time is fixed at 10 min to prevent the anatase–rutile phase transformation (Licciulli, et al.,2011)

2.2 Colloidal synthesis of TiO_2 nanorods by hot injection

TiO_2 nanorods (100% anatase) have been synthesized by hydrolysis of TTIP (titanium tetraisopropoxide 99.999%, from Aldrich) using technical grade oleic acid ($C_{18}H_{33}CO_2H$ or OLEA) as a surfactant at low temperatures (100 °C) as reported elsewhere.(Cozzoli, et al.,2003) Briefly, the synthesis involves the hydrolysis of TTIP catalyzed by trimethylamino-N-oxide dihydrate solution ($(CH_3)_3NO_3$ $2H_2O$ or TMAO, 98%) in presence of large excess of water. OLEA-coated anatase TiO_2 NRs (20×3 nm) have been readily precipitated upon addition of an excess of ethanol, recovered by centrifugation and washed three times with ethanol to remove the excess of OLEA. At this stage, OLEA capped TiO_2 NRs have been easily re-dispersed in $CHCl_3$, without any further growth or irreversible aggregation and then properly diluted for the stone treatments.

2.3 Stone samples

The two different lithotypes, "Pietra Leccese" (PL) and "Pietra di Trani" (PT), that have been selected for being investigated in this work, are mainly composed by calcite minerals with a negligible insoluble residue. However PL and PT are very different in terms of porosity, such a feature then represent a relevant parameter influencing the effectiveness of their surface treatment. In particular, PT has an open porosity measuring 4% ca., while PL is characterized by a high porosity ranging from 30-to 40% (Licciulli, et al.,2011).

2.4 Application of the coatings on stone

All stone samples have been cut into 5×2×1 cm slabs and one 5×2 side of each sample has been treated.

After removal of dust deposits by means of a soft brush, the stone specimens PL and PT have been rinsed with deionized water, and dried at 60°C until the difference between two consecutive weighing measurements was less than 0.1% of the original weight of the stone samples.

Two different treatments have been carried out. In the first, hydrothermal TiO_2 has been applied by spray coating on PL and PT, while the TiO_2 nanorods have been deposited by drop casting only on a PL sample.

The hydrothermal nano-TiO_2 sol has been applied by spray coating a nano-TiO_2 based dispersion on PL and PT by means of an HPLV (High Volume Low Pressure) spray gun with a 0,8 mm diameter nozzle. The stone specimen treated with hydrothermal nano-TiO_2 are labeled as PL_{HT} and PT_{HT}.

The TiO_2 nanorods on PL samples have been deposited by casting of 150 µL of a 0.05M chloroform solution of TiO_2 nanorods. Hereafter, such stone specimens will be referred as $PL_{NR.}$

After the treatments the stone specimens have been kept in a desiccator to prevent humidity accumulation.

2.5 Static contact angle measurements

Measurements have been performed by using a Costech contact angle measuring instrument (NORMALRec33/89,Rome 1989).

2.6 Colorimetric measurements

These tests have been performed by means of a Minolta CR 300 Chroma Meter reflectance colorimeter to evaluate the color changes. (CIEStandardS014-4/E:2007,1976, NORMALRec43/93,1993)

The effect of TiO_2 based treatments on the aesthetical properties of stone specimens has been investigated by the CIELab method. The method exploits three different coordinates in order to define objectively a color: L*, which corresponds to the brightness, a* corresponding to the red-green color intensity, and b* corresponding yellow-blue color intensity.

The chromatic variations with reference to the color parameters of the stone surface before and after the application of the treatments are expressed as:

$$\Delta E^* = \lfloor (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \rfloor \qquad \text{eq.1}$$

2.7 Determination of TiO_2 leaching from stone

In order to assess possible TiO_2 leaching from stones in presence of water and light the samples, after the application of the coatings, have been immersed in water for 3h. The resulting solutions have been analyzed for determination of dissolved Ti concentrations by using graphite furnace absorption spectroscopy using GFS97 instrumentation (Thermo).

2.8 Photocatalysis experiments

In order to investigate the self cleaning properties of PL_{HT}, PT_{HT} and PL_{NR}, photocatalysis experiments have been performed at treated stone-air interface. Treated stone specimens have been stained with 100 µl of Methyl Red solution (2-(4-dimethylamino-phenyl-azo)-benzoic acid, C. I. 13020 or MR) $3.5 \cdot 10^{-3}$ M dissolved in isopropanol. The stained stone specimens have been let to dry for 12 h and subsequently exposed to a solar light simulator, ORIEL Instruments, equipped with a Xenon arc lamp, with a power of 150W, and a light flux of 0.0455 W/cm^2 corresponding to 0.33 SUN.

At a fixed illumination time, the irradiation has been stopped, and the total reflectance spectra of the stained stone have been registered in order to monitor the degradation course of the model dye.

Dye decoloration has been estimated by measuring the absorbance intensity at the maximum wavelength of the dye (430 nm) according to the equation 2:

$$\frac{A_{t=0} - A_{t=t}}{A_{t=0}} \qquad \text{eq 2}$$

Reflectance spectra have been carried out with UV Vis-near IR Cary 5 (Varian) spectrophotometer equipped with an integrating sphere.

3. Results and discussion

3.1 Characterization of coated stone specimens

The stone specimens have been characterized before and after coating deposition by colorimetric measurements, and static contact angle measurements. The main characteristics of the specimens after coating deposition are reported in Table 1.

Colorimetric results have showed acceptable color variations after the treatment with both hydrothermal TiO_2 nanocrystals and TiO_2 nanorods (Table 1).

In order to assess the wettability properties of the stone specimens after each treatment, static contact angle measurements have been performed, in order to detect possible change in the contact angle upon coating applications.

For PL_{HT} and PT_{HT} samples, no effect of the treatments has been detected by contact angle measurements. The contact angle value, indicative for a hydrophilic surface, has remained unchanged in the case of the PT_{HT}. On the other hand, due to the high porosity of PL samples, the contact angle has not been recorded as the water drop has been quickly adsorbed by the stone for both untreated and hydrothermal TiO_2 coated samples, thus preventing the measurement to be performed.

Table 1. Characterization of stone samples: mass of catalyst, static contact angle values ± standard deviation, color variations. (CIEStandardS014-4/E:2007,1976).

Samples	mg TiO_2	mg/cm^2	α±sd b.t.	α±sd a.t.	ΔE
PL_{HT}	0.54	0.054	n.d.	n.d.	2.10
PT_{HT}	0.42	0.042	54 ± 8	53 ± 9	1.24
PL_{NR}	0.60	0.060	n.d.	132±8	3.64

b.t. = before treatment; a.t. = after treatment; n.d. = not determined

On the contrary, contact angle measurements performed on PL_{NR} sample have recorded a value of 132±8° which is consistent with a hydrophobic surface. This result suggest that the OLEA-capped TiO_2 nanorods confer hydrophobicity to the stone surface.

3.2 Absorption of a model dye in aqueous solution

The resistance against the water penetration of the two TiO_2 based coatings on PL have been compared. PL_{HT} and PL_{NR}, have been immersed in an aqueous solution of MR ($3.5*10^{-5}$M, pH 6.5) for 3h, under stirring, in the dark.

Afterwards, the stone specimens have been removed from the MR solution and let to dry at the dark. Total reflectance spectra have been recorded and compared with the total reflectance spectra of the respective stone specimen before the experiment (Figure 1). Under such experimental conditions MR aqueous solution is able, first of all, to probe stone wettability.

The broad band below 400 nm, present in all the sample, could be ascribed to the presence of TiO_2 coatings. After the immersion in MR solution in the dark, the reflectance spectrum of PL_{HR} has showed an increase in the absorption signals, along the whole investigated spectral range, and, mainly, in the region between 400 and 500 nm. The increase in the absorption signals could be ascribed to the presence of water molecules adsorbed on the stone surface.. Therefore, it is reasonable to infer that the PL_{HT} can absorb water or dye molecules dissolved in water solution, despite the treatment with hydrothermal TiO_2. Indeed it must be taken into account that static contact angle measurement could not be performed on the PL_{HT} stone as the coating cannot prevent water drop adsorption (Table 1).

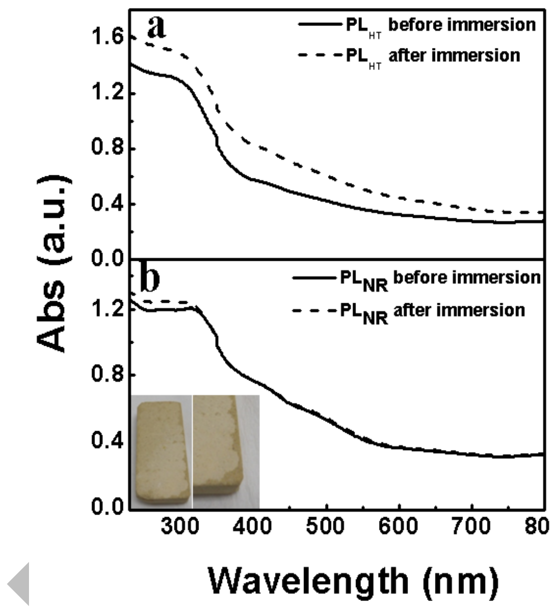

Figure 1. Total reflectance spectra recorded before (solid lines) and after (dashed lines) the immersion in MR solution at dark, for PL_{HT} sample (a) and PL_{NR} sample (b) The inset of Fig. 1b shows a photograph of PL_{NR} after the immersion in the aqueous solution of MR at dark. The magnification points out how in the corner of the sample is possible to distinguish the TiO_2 nanorod treated region from the accidentally untreated one.

Conversely, after the immersion in MR at dark, the reflectance spectrum of PL_{NR} sample, has strongly resembled to that of the sample prior to the immersion in MR. No absorption signals ascribable to water or MR has been observed. Such a result is consistent with the contact angle measurements, thus suggesting that TiO_2 nanorod based coating could confer a hydrophobic character to the PL surface.

A further evidence of such a behavior is shown in the inset of Fig 1b, reporting a photograph of a PL_{NR} sample. The edges of the PL stone specimen, accidentally not covered with TiO_2 nanorods, appear darker due to MR molecules absorbed, while the stone surface treated with TiO_2 nanorods remainalmost unchanged with respect to the original appearance.

Such results are in good agreement with contact angle measurements and reasonably support the indication that the different surface chemistry of TiO_2 nanoparticles, prepared by the two distinct synthetic strategies, can affect the surface properties of the treated stones.

In fact, hydrothermal TiO_2 consisting of nanoparticles with an average size of 3.5 nm, without any capping agent (Licciulli, et al.,2011), expose OH groups at their surface, thus providing a hydrophilic character to the coating on PL. On the other hand, TiO_2 nanorods are capped by OLEA molecules, possessing a polar moiety able to coordinate the surface OH groups of TiO_2 nanorods and a hydrophobic tail exposed outward, ultimately endowing a hydrophobic character to TiO_2 nanorods, and, consequently to the PL_{NR} surface where they are applied.

3.3 Stability of coating against water exposure and solar illumination

The stability of the TiO_2 coatings against water and light has been investigated by dipping each stone in water (pH 6.5) and irradiating the sample with a solar light simulator for 3h under stirring. Subsequently, the water solution has been analyzed by Atomic Absorption Spectroscopy (AAS) to detect concentration of Ti species possibly released in water

For all investigated cases the amount of TiO_2 leached in the solution represents a negligible fraction of the total TiO_2 content of each coating, indicating a good stability of the TiO_2 based coatings under the investigated conditions (Table 2).

Table 2. AAS for determination of Ti, on aqueous solution after 3h of irradiation

Sample list	Ti Concentration (μg/L)	% TiO_2 in solution
PL_{HT}	15.63	0,1
PT_{HT}	1.490	0,01
PL_{NR}	0.940	0.003

3.4 Photocatalysis tests

Photocatalysis experiments have been performed at solid-air interface, in order to investigate the self cleaning properties, of the coatings exposed to a solar light simulator. In particular hydrothermal TiO_2 nanocrystals have been tested on a PT sample, while TiO_2 nanorods have been tested on a PL sample. A solution of MR in isopropanol has been used as staining agent, to simulate a generic pollution on the stone surfaces. In particular the MR solution used as staining agent represents a convenient choice, because its degradation mechanism has been extensively studied and it is thus possible to obtain reliable information on the photodegradation course (Comparelli, et al.,2005, Petronella, et al.,2011). Photocatalysis experiments have been monitored by recording total reflectance spectra at scheduled time intervals. In order to obtain a selective

identification of MR signals, the reflectance spectra have been recorded in absorption mode, using the reflectance spectra of the treated stones, as a reference.
Photocatalytic tests have been typically carried out for 6 h and the main absorption peak of MR has been monitored at 430 nm, by applying, then, the eq. 2 to calculate the decolouration percentage. Reported data are presented as mean values ± standard deviation, calculated from the analysis of three replicates.
Fig. 2 shows that both hydrothermal nano-TiO_2 on PT and TiO_2 nanorods on PL have exhibited a significant photocatalytic activity in the dye degradation. During the first hour of irradiation, the degradation percentage have been above 50 percent, afterwards the decoloration percentage has increased more slowly.

The obtained results suggest that the both the TiO_2 based treatments are able to confer self cleaning properties to the investigated stone specimens

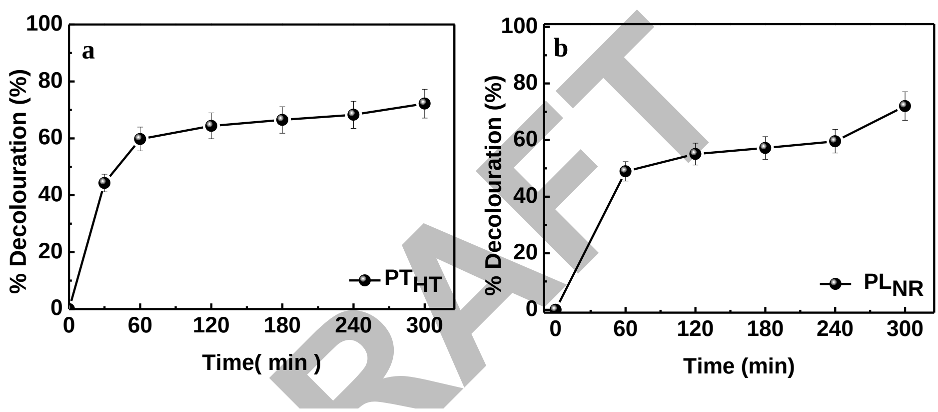

Figure 2. Time course evolution of decoloration of MR value for PT_{HT} (a), and PL_{NR} (b), respectively, evaluated by monitoring the absorbance intensity at 430 nm from total reflectance spectra.

4. Conclusions

In this work, two different nanosized semiconductors, namely hydrothermal TiO_2 nanocrystals and TiO_2 nanorods have been synthesized exploiting an hydrothermal method and the "hot injection technique" respectively.

The two nanostructured materials have been applied on two types of stones, with the same carbonatic composition, but with different porosity "Pietra Leccese" (PL) and "Pietra di Trani"(PT). The investigation of the physical characteristics of both the nano-TiO_2 based coatings applied on porous and compact calcareous stones, which are both widely used within stone buildings of the cultural heritage has been carried out.

Experimental results have revealed that both nano-TiO_2 based coatings are rather stable under the investigated conditions, and the application of the nanoTiO_2 based coatings does not significantly affect the aesthetical characteristics of the investigated stone specimens. Interestingly, TiO_2 nanorods have been demonstrated to convey a hydrophobic behavior to PL, probably due to the presence of oleic acid molecules coordinating the surface of TiO_2 nanorods.

Finally the photocatalytic activity of hydrothermal TiO_2 and TiO_2 nanorods has been tested at solid/air interface, using the azo dye Methyl Red as target compound, in order to simulate a form of deterioration and pollution. Photocatalysis tests have revealed that both TiO_2 nanorods and hydrothermal TiO_2 nanocrystals are interestingcandidates to endow a self-cleaning behavior and to provide a protective coating to the stone specimens, under the investigated conditions.

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