

Photoactive semiconductor nanocrystals for surface protection of architectural stone

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Summary. — The unique size-dependent chemical-physical properties of semiconductor nanocrystals can be profitably applied to the field of cultural heritage protection. The present paper accounts for the realization of colloidal TiO₂ nanocrystals based coatings, with controlled morphology, with the goal to convey new functional properties to the surfaces of monuments and buildings of cultural interest. In the present paper, we collected the chemical-physical characterization and the investigation of the photocatalytic activity of rod-like TiO₂ nanocrystals (TiO₂NRs) based coatings applied to the *Pietra Leccese*, a porous calcarenite stone, extensively used in Southern Italy monuments. The application of TiO₂ NRs based coatings was realized by three different techniques: casting, dipping and spray-coating. The coating resulted in a functional protective layer, with self-cleaning characteristics, as demonstrated by its photocatalytic activity, enabling a new generation of smart coatings.

1. – Introduction

In recent years, the great advances in nanomaterial science are opening up original opportunities in the field of cultural heritage protection [1]. Relevant cases are represented by nanosized TiO₂ based coatings, which resulted to be promising alternatives with respect to conventional polymeric coatings for the protection of monuments and buildings of historical and cultural interest against environmental pollution [2]. Polymeric coatings, such as acrylic, fluorinated and alkoxy silanes, although effective for the protection of monuments, have reported drawbacks including loss of adhesion and drop in protection performance, sensitivity to weathering and chemical aging, that can induce photo-oxidative irreversible modifications [3] or yellowing [4]. In contrast, several studies have demonstrated the potential of TiO₂ nanoparticles (NPs) based coatings as protective layer for stony surfaces [5-7]. Indeed, TiO₂ NPs based coatings were found to be able

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to prevent biodeterioration of stony surfaces [5,8] and, thanks to their combined photocatalytic and hydrophobic properties, to decrease the formation of black crusts [9], and deposition of salts (Cl^- , NO_3^- , SO_4^{2-}) [10], and to convey hydrophobic properties to the stony surfaces, without affecting the aesthetic characteristics [11]. Further, TiO_2 NPs present peculiar features, including an extremely high surface area, chemical stability [12] unique surface properties, as the photoinduced superhydrophilicity and high photoactivity [11,13]. Indeed, under light irradiation of suitable wavelength, TiO_2 NPs promote the formation of electron/hole pairs (e^-/h^+) which, once migrated to the TiO_2 NP surface, react with adsorbed O_2 or H_2O molecules, thus triggering the production of reactive oxygen species (ROS), able to promote degradation and, potentially, the mineralization organic pollutants, both in water and at the solid/air interface [14,15]. Several examples report on the use of TiO_2 NPs applied on stone surfaces for preservation and conservation purposes. These examples include both the direct application of TiO_2 NPs on stone surfaces [16,17] as well as the application of TiO_2 NPs embedded in polymeric matrices in order to obtain functional coatings [18].

The present paper aims at reviewing the results obtained on the fabrication, characterization and application of rod-shaped TiO_2 nanocrystals, anatase in phase, as self-cleaning and hydrophobic coating to be applied to the surface of *Pietra Leccese* (PL), a building material typical of artistically relevant Baroque monuments in the Apulia region (Southern Italy) [16,17]. TiO_2 nanorods (NRs) have been taken into account, as such nanosized photocatalysts may offer unique advantages, as photocatalytic functions and surface properties, that may result particularly valuable in the field of monument conservation. TiO_2 NRs, synthesized by using a colloidal chemistry route, are anatase in phase with 18 nm in length and 3 nm in diameter, and show a specific surface area of $240 \text{ m}^2/\text{g}$ [19]. The high control on size and shape was provided by the oleic acid (OLEA) molecules, that also coordinated the surface of the NRs preventing their aggregation and allowing their dispersibility in low-polarity organic solvents. OLEA capped TiO_2 NRs dispersed in apolar solvents result in optically clear dispersions and are, thus, highly processable and suitable to be incorporated in formulations, including appropriate polymeric matrices [20]. TiO_2 NRs possess unique structural and morphological properties responsible of their high photoactivity. Indeed, the anatase phase of the TiO_2 NRs along with their peculiar anisotropy were found effective in increasing the lifetime of the photogenerated e^-/h^+ [21]. Further, the OLEA molecules, coordinating the TiO_2 NRs with the carboxylic moiety, exposing the alkyl chain to the outside, proved to be able to make the stone surface hydrophobic [16]. Here, the preparation of TiO_2 NRs based formulations and the main results of their application to PL samples are reported, discussing in details the photocatalytic performance of the TiO_2 NRs based coatings.

2. – Synthesis and characterization of TiO_2 nanorods

The TiO_2 NRs were synthesized by hydrolysis and polycondensation of titanium tetraisopropoxide (TTIP), according to the procedure reported in [20]. Hydrolysis of TTIP was achieved by injecting a suitable amount of trimethylamino-N-oxide dihydrate (TMAO) dissolved in water, in a reaction flask containing technical-grade OLEA as coordinating solvent at a temperature in the range from $80 \text{ }^\circ\text{C}$ to $100 \text{ }^\circ\text{C}$. The growth of TiO_2 NRs required 5 days and was performed in nitrogen atmosphere. Subsequently, TiO_2 NRs were collected by precipitation, adding an excess of ethanol, isolated by centrifugation and washed three times with ethanol and chloroform to remove the excess of OLEA. The obtained OLEA-capped TiO_2 NRs were easily re-dispersed in organic solvents with

low polarity. The presence of OLEA as coordinating agent for TiO₂ NRs resulted in an optically clear dispersion, without aggregates or suspended matters.

The morphological characterization of the obtained product was performed by TEM microscopy. The TEM micrograph of the nanostructures reported in fig. 1(a) shows anisotropic particles with an average dimensions of 18 × 3 nm. The results of X-ray diffraction (XRD) analysis in fig. 1(b) are compatible with the presence of anatase phase. The anisotropy in the obtained NPs clearly assessed by the reflection at 2θ = 37.86° corresponding to the {004} plane that is more intense and sharper with respect to {200} and the {211} reflections at 2θ = 48.6° and 2θ = 55.09°, respectively. Further, the two signals at 2θ = 30° and 2θ = 33° suggest the presence of a brookite phase too [17, 20]. A rational solvent selection is essential in order to form a high-quality coating that turns to be uniform, crack-free, transparent, reproducible and stable after application. The surface chemistry of TiO₂ NRs was investigated by FT-IR-ATR, and the results are reported in fig. 1(c). The obtained spectrum provides substantial insight for the solvent selection. Interestingly the typical signal between 1760 and 1765 cm⁻¹, associated to the carbonyl group stretching, could not be detected, thus suggesting that Ti sites at the surface of TiO₂ NRs are involved in a chelating bidentate complex with carboxylic group of OLEA. Such evidence is further supported by the presence of the two absorption peaks at 1527 cm⁻¹ and 1463 cm⁻¹ that are compatible with the occurrence of complexes of COO⁻ group with Ti centers [22]. In summary, OLEA molecules coordinate the surface of TiO₂ NRs through the carbonyl group, exposing the hydrophobic chain outward, thus providing colloidal stability in low-polarity organic solvents. Therefore, chloroform [16] and n-heptane [17] were selected as suitable solvents for application of TiO₂ NRs based coatings by casting, dipping and spray coating, respectively.

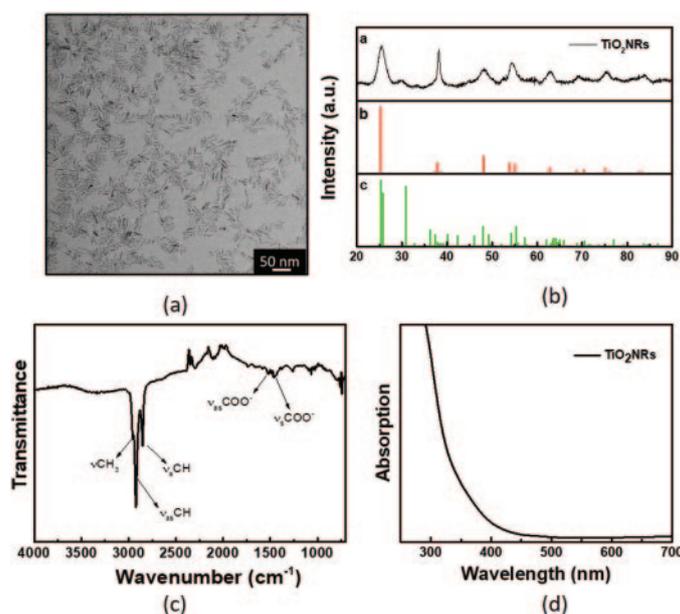


Fig. 1. – Characterization of TiO₂ NRs by TEM microscopy (a), XRD analysis (b), FTIR spectroscopy (c) and UV-Vis absorption spectroscopy (d). Reprinted with permission from ref. [17].

3. – Application and characterization of TiO₂ NRs on Pietra Leccese surfaces

The direct application of TiO₂ NRs on PL was preferred because it enables a full interaction between the photocatalyst and the PL surface and, therefore, a prompt evaluation of TiO₂ NRs photocatalytic activity is possible. The direct application of TiO₂ NRs was carried out by three techniques: casting, dipping [16,17] and spray coatings [17]. Casting was selected because it simulates a brush type of application with the advantage of controlling the amount of photocatalyst on the stone surface, thus allowing a rational evaluation of the photocatalytic activity. It essentially consists in the dropwise spreading of the defined amount of TiO₂ NRs dispersed in chloroform on the PL surface. Dipping relies on the immersion of the PL sample in a chloroform dispersion of TiO₂ NRs. Dispersions of TiO₂ NRs at different molar concentration were used. Clearly, application by dipping can be only performed onto small artefacts or, as a preliminary treatment, on the stone blocks to be used later for buildings or artefacts [16]. Spray coating is a promising application technique, suited for large-scale application, which proved able to result into high-quality, crack-free and stable coatings on the stone surface [23,24]. A systematic investigation, as a function of spraying time, was preliminarily carried out on silicon chips in order to define the most appropriate solvent to be used to disperse TiO₂ NRs for performing a spray coating treatment [17]. The experimental conditions most suited for application of TiO₂ NRs by casting (5 μ mol of TiO₂ NRs), dipping (TiO₂ NRs 0.05 M) and spraying (spraying time 1 min from an eptane solution) were investigated and the results are reported in table I along with the outcome of the chemical-physical investigation. As the preservation of the aesthetical features is an essential requirement for monument conservation, the color variation upon the application of coating was carefully assessed by ΔE measurements, in compliance with the current national European regulation (UNI EN 15886, 2010) [25]. The results are reported in table I and show that ΔE values lay under the ΔE value generally accepted in the field of stony monument conservation, $\Delta E < 5$ [2]. The effect of TiO₂ based coatings on the wettability of stony material is a relevant issue for preserving architectural stone surfaces, because water penetration is one of the most harmful causes of stone decay, being also able to finally induce biological deterioration [2]. Therefore, static water contact angle measurements were performed indicating that, while uncoated PL stones are extremely porous, presenting such fast absorption of water droplets to prevent any measure of contact angle, the application of TiO₂ NRs based coatings, irrespectively of the application method (table I) proved able to convey a hydrophobic character to the PL surface showing a static contact angle value up to 144°. Such a behavior can be safely associated to the

TABLE I. – *Main chemical-physical features of TiO₂ NRs-based coatings applied on Pietra Leccese by casting, dipping and spraying. Reprinted with permission from refs. [16,17].*

Sample	Application technique	ΔE	Static contact angle	Water vapour permeability (%)
PBLc 3	casting	1.57 ± 0.05	$144^\circ \pm 5$	8.9
PBLd3	dipping	1.32 ± 0.04	$134^\circ \pm 4$	-11.5
PLA	spray coating	0.18 ± 0.08	$130^\circ \pm 10$	-19

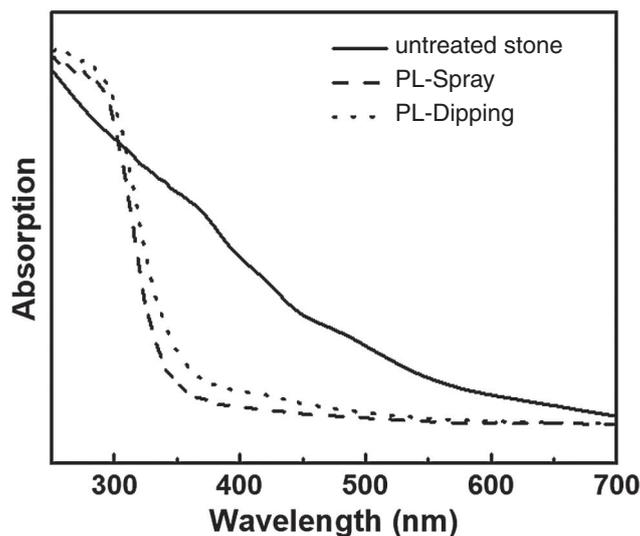


Fig. 2. – Characterization of TiO_2 NRs by diffuse reflectance spectroscopy. The reflectance spectra, reported as the Kubelka-Munk function, compare the untreated stone (solid line) with the coating achieved by spray (dashed line) and dipping (dotted line), respectively. Reprinted with permission from refs. [16, 17].

presence of OLEA at the surface of TiO_2 NRs [26]. Since a sustainable coating should not act as a barrier, allowing, instead, the water vapor migration outwards, the water vapour permeability is an additional essential parameter to be assessed [17]. The direct application of TiO_2 NRs by casting, dipping and spray mainly resulted only in a slight decrease of water vapour permeability, still in the range of the original characteristics of the stone [17]. In most of the cases the direct application of TiO_2 NRs by casting, dipping and spray produced a slight decrease of water vapour permeability which is still compatible with the original permeability properties of the stone [16]. An example is the PL specimen treated by spray coating for 1 min which produced a 19% decrease of water vapour permeability (table I) [17].

A qualitative evidence of the presence of TiO_2 NRs based coatings is pointed out by the results of the reflectance spectroscopy investigation and by SEM/EDS analysis, that are reported in fig. 2 and fig. 3, respectively. Figure 2 shows the typical increase in the absorption below 400 nm indicating the indirect allowed transition of TiO_2 NCs [27]. Figure 3 clearly highlights the differences in morphology and chemical composition of PL after the application of TiO_2 NRs based coatings.

4. – Outdoor photocatalytic activity of TiO_2 NRs based coatings

The photocatalytic activity of TiO_2 NRs based coatings was reported under several experimental conditions including different light sources for indoor experiments [16], and different weather conditions for outdoor experiments [17]. Remarkably, in all investigated conditions and irrespectively on the application methods, TiO_2 NRs based coatings proved to be photoactive. PL samples prepared by casting and dipping showed a complete MR stain decolouration after 24 h of irradiation under a solar light simulator (fig. 4) [16].

Figure 4 reports the photocatalytic investigation under the irradiation of a solar light

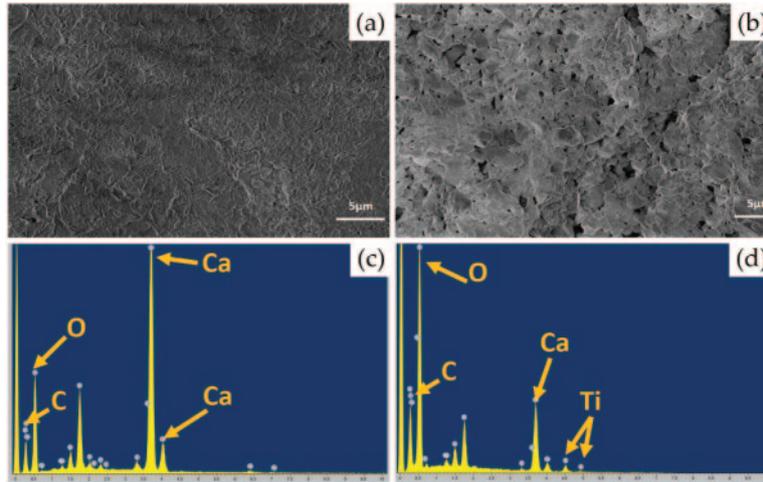


Fig. 3. – SEM micrographs of untreated (A) PL stone and PL-D (B) treated by spray coating and corresponding EDS spectra (C and D). The SEM measurements were performed with an accelerating voltage of 1KV, a working distance of 3.7mm and an aperture size of 20 μm. Reprinted with permission from ref. [17].

simulator carried out on the PL samples prepared by casting and dipping as a function of the TiO₂ NRs amount in the applied dispersion [16]. The PL samples coated by casting and dipping showed a complete MR stain decolouration after 24 h of irradiation under a solar light simulator (fig. 4). The photocatalytic activity of the spray-coated PL sample was assessed in outdoor experiments. In this case, the complete MR decolouration was detected after one week of outdoor exposure (fig. 5). Moreover, TiO₂ NRs retained their photocatalytic activity also upon incorporation in a UV-Vis-light curable hybrid methacrylic siloxane resin [28], resulting in the ability of the resulting nanocomposite of achieving a MR decolouration of 34% after 24 h of UV light irradiation and of 56% after one week of exposure outdoor, as reported in ref. [18]. What is more, in this case the durability assessment experiments revealed that after 12 months of outdoor exposure the nanocomposite coated PL preserved the hydrophobicity and the ΔE value [18].

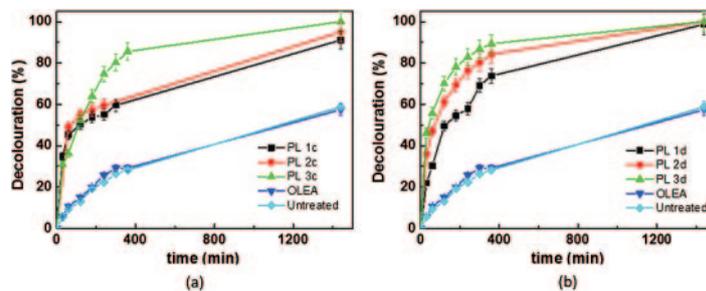


Fig. 4. – (a) Photocatalytic decolouration of Methyl Red (MR) calculated for all PL samples treated by casting (a) and dipping (b), as a function of amount of TiO₂ NRs amount and TiO₂ NRs dispersion concentration, respectively. The photocatalysis experiments were performed under a solar light simulator for 24 h of irradiation. An untreated PL sample and a sample treated with OLEA were considered as reference. Reprinted with permission from ref. [16].

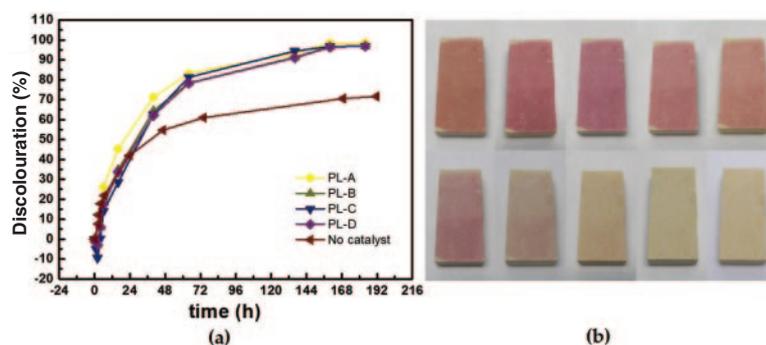


Fig. 5. – (a) Photocatalytic discoloration of Methyl Red (MR) calculated for all TiO₂ NRs coated PL samples as a function of the spraying time. The photocatalysis experiments were performed outdoor for 192 h. An untreated PL sample was used as a reference. Reported data are presented as mean values standard deviation obtained from the analysis of two replicates. (b) Upper row: pictures of the PL-D sample taken at: 0 h, 2 h, 4 h, 6 h, 16 h of irradiation during the outdoor exposure for 192 h respectively. Lower row: pictures of the PL-D sample taken at: 40 h, 64 h, 136 h, 160 h, 192 h of irradiation respectively, during the outdoor exposition for 192 h. Reprinted with permission from ref. [17].

Despite the high energy gap of anatase TiO₂ nanoparticles (3.2 eV, 384 nm), in all reported cases of study, the TiO₂ NRs based coatings demonstrated a high photocatalytic activity both under solar light simulator and in outdoor photocatalysis experiments. The ensemble of these results can be accounted for by the high photocatalytic activity of TiO₂ NRs at the solid/air interface, demonstrating that the reduced UV fraction of the solar spectrum is sufficient to promote the photogeneration of e⁻/h⁺ pairs. Such promising performances are also due to the interplay of several parameters, including the high specific surface area of TiO₂ NRs [19], the high degree of crystallinity [20], the peculiar anisotropic geometry that contributes to minimizing the detrimental e⁻/h⁺ pairs recombination events [21]. Also the unique TiO₂ NRs surface chemistry plays an important role as the coordination bond between surface –OH groups of TiO₂ NRs and OLEA allows to stabilize the photo-induced excited state of TiO₂ NRs [29]. Interestingly, the photocatalysis experiments carried out on the TiO₂ NRs coated samples prepared by casting, dipping and spraying, showed an increase in the photocatalytic activity with the decrease in the amount of deposited TiO₂ NRs. Such a result was explained considering that a low amount of photocatalyst can result in a more homogeneous distribution of TiO₂ NRs and in a larger amount of the exposed surface-active sites, that result available for the adsorption of the target molecules and for the production of reactive radicals [30].

5. – Conclusions

This work aims at summarizing the experimental results relative to the direct application of TiO₂ NRs to the surface of *Pietra Leccese*, with the final goal of conveying to the stone hydrophobic and photocatalytic properties. TiO₂ NRs were prepared by using a colloidal synthetic route able to provide anisotropic nanoparticles with a peculiar surface chemistry characterized by the presence of the OLEA molecules coordinating the TiO₂ NRs. Such a feature makes the colloidal TiO₂ NRs stable in a polar organic solvent, thus allowing their application on the *Pietra Leccese* surface, by using different

reproducible and controlled application treatment. The TiO₂ NRs based coating were applied by casting, dipping and spraying, after a careful selection of the proper solvent. Overall, the resulting coated stone samples preserved their original aesthetical features presenting, in addition, hydrophobic and photocatalytic properties. In this perspective, although relevant issues, including long-term stability and photocatalytic efficiency with respect to specific real contamination, need to be carefully investigated, TiO₂ NRs based coatings are very promising for the development of a suitable formulation to be applied for the conservation of buildings and monuments.

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