Application of a new photocatalytic nanomaterial obtained by Pulse Laser Ablation for Polychrome Paintings Conservation: a feasibility study

Stefania Pasquale[1]; Vittorio Privitera[2]; Maria Miritello[2]; Massimo Zimbone[2]; Giuseppe Politi[1]; Anna Maria Gueli[1]

[1] Catania University, Physics and Astronomy Department "Ettore Majorana", PH3DRA Labs & CHNet- INFN sec CT, Catania, Italy

[2] Consiglio Nazionale delle Ricerche - Institute for Microelectronics and Microsystems, Catania, Italy

Abstract

This works aims to present a preliminary study about the application on painting of TiO_2 nanoparticles for self-cleaning and protective purposes. We firstly assessed the photocatalytic activity of the TiO_2 nanoparticles, obtained by Pulsed Laser Ablation, by the discoloration of dye. After, the colloidal dispersion is applied to painting samples prepared in laboratory, according to old recipes and using the most-used historical binders and pigments, in order to verify the cleaning efficiency by discoloration of the chromatic markers. The spectrophotometric analysis is performed studying the Spectral Reflectance Factor trend and the color coordinates.

Keywords

Conservation, Cleaning, Protection, Nanomaterial, Easel painting, Titanium dioxide.

Introduction

Conservation science is one of the most complex topics in materials science, as it requires interdisciplinary expertise. Especially easel paintings are still today one of the challenges in conservation and restoration of cultural heritage. This is due to the composite structure, built up from canvas and/or wood, ground, paint, and varnish layers, constituted by both organic and inorganic materials. This complexity requires skills acquired through extensive training and practical experience, especially in the cleaning intervention. Conservators face a difficult decision when selecting a methodology for cleaning painted surfaces because permanent damage can easily result from even the most careful attempts to clean a painting by untrained personnel or by non-adequate materials. According to the most used methodologies, restorers can clean by mechanical means, by organic solvents or alkali-based aqueous cleaning solutions. Considering all these methods, cleaning represents an irreversible treatment and for this reason, it would be better to adopt certain measures that can prevent or slow down the accumulation of dirt and dust that represent the first phase in deterioration painting surface.

Recent developments have shown that the complex tasks of cultural heritage conservation can be solved very effectively using novel nanomaterials and nanotechnology methods. Over the last years, the interest in the production and use of new nanostructure materials in cultural heritage conservation has been growing (Quagliarini, 2018; Baglioni, 2015; Munafò, 2015; La Russa, 2016; Bergamonti, 2017; Ion, 2019). About paintings, many

products with different characteristics were developed for removing dirt and dust films from the surfaces and for providing effective cleaning by reducing the solvent permeation into underlying paint layers and many harmless products. The discussion on how to improve nanotechnology regards only wall paintings and it is dealt with by research projects such as Nanoforart (Giorgi, 2010).

This paper is aimed at assessing new nanomaterials alternative to traditional conservation treatments. On this occasion, we present a preliminary study regarding the application on paintings of a material constituted by titania nanoparticles to test its self-cleaning performances.

In the last years, self-cleaning titanium oxide efficiency was tested on different materials belonging to Cultural Heritage, with good results especially stone (Hosseini, 2018). About the use of titanium dioxide on paintings, different positions are discussed. It was proposed that TiO_2 has both positive and negative influences on paint film durability. On one hand, adding TiO_2 to a specific paint may improve its durability due to TiO_2 protection and self-cleaning, but on the other hand, it may affect negatively the paint due to photocatalytic degradation of the organic components. According to some studies, TiO_2 affects paint durability especially if it is used as a pigment in paintings (Van Driel, 2016, 2017, 2018, 2019).

In our study, TiO_2 nanoparticles are obtained by Pulsed Laser Ablation in Liquids (PLAL). This high-power laser pulse technique is focused on a solid target immersed in water. Local temperature rise creates a plasma plume that expands in the liquid. The subsequent cool down of the temperature due to the presence of liquid water releases nanoparticles in solution. PLAL represents a versatile, economical and "green" methodology to produce nanoparticles. It avoids the use of chemical reagents, solving the problem of purification of nanomaterials. For these reasons, the PLAL represents one of the most promising techniques for the synthesis of nanoparticles in liquids or polymeric matrices. This technology takes advantage of the easy handling with low risk and no chemical processing waste is produced but at the same time, the final properties of the metal nanoparticles are strongly dependent on the experimental set up (Sadrolhosseini, 2019).

The photocatalytic activity of laser-ablated titanium dioxide nanoparticles is assessed by Methylene Blue dye discoloration method. Comparison with commercial TiO_2 is made using UV-VIS spectrophotometric technique (according to the standard (Mills, 2012)) and also by colorimetric measurements through the color difference assessed by *Commission Internationale de l'Ecleraige* (CIE). The CIE standard is often employed for testing the photocatalytic activity in many materials belonging to cultural heritage (Oleari, 2016, Bergamonti, 2013, Munafò, 2015). In these cases, the quantification of CIE color difference in fact can represent a tool for evaluating the dye discoloration.

The paintings are laboratory prepared, using historical vehicles and pigments according to old recipes. For evaluating the efficiency in terms of cleaning performance of the TiO_2, the samples are dirtied with specific material and then irradiated by UV at different times in a

Color Assessment Cabinet. The photo-degradation on paintings is evaluated by spectro-photometric analysis considering the Spectral Reflectance Factor trend and the colorimetric coordinates, according to the European standardization (EN1586:2010). Furthermore, in order to evaluate the titanium distribution, PIXE mapping is performed on the painting samples.

Materials and Methods

The colloidal dispersion preparation

The synthesis of Laser Ablated (LA) nanoparticles was performed according to reference (Zimbone, 2015 2016 a,b, Cacciato, 2016) Briefly A Nd:YAG (Giant G790-30) 1064 nm laser (10 ns pulse duration, 10Hz repetition rate) was employed to irradiate titanium metal plate (Goodfellow, purity 99.99% as rolled). The laser was focused using a lens (focal length of 15 cm); on the bottom of a Teflon vessel filled with 5 ml of deionized Milli-Q water (resistivity 18 MΩc). The sample was irradiated at a fluence of 5 J/cm^2 and the spot size was about 3.5 mm in diameter. The mass of the ablated material was estimated by weighting the target before and after the ablation with a micro-analytical balance with a sensitivity of 100 μg. The titanium concentration in solution was calculated assuming that ablated material (1 mg) has been totally converted into nanoparticles in 5 ml of water. The prepared dispersed titania particles have a Feret diameter of 30 nm and are composed of a mixture of small crystallites and disordered TiO_2 (Zimbone, 2015).

Commercial standard TiO_2 nanoparticles by Sigma-Aldrich (SA) were used as a reference for the discoloration experiments. Nanoparticle size is lower than 100 nm. The prepared solution is obtained by dissolving 8 mg of powder in 8 ml of Milli-Q water (final concentration of 1 mg/ml) and stirring for 30 min.

In the following sections, we called Laser Ablated TiO_2 nanoparticles as LA-TiO_2 NPs and TiO_2 nanoparticles by Sigma-Aldrich as SA-TiO_2 NPs. We use also an acronym CD for designating the Colloidal Dispersion.

The painting samples

Ten paintings were prepared in the laboratory mixing yellow and blue pigments (yellow ochre and lapis lazuli) with egg tempera medium with a fixed ratio equal to 1:3 between powdered pigment and wet medium, according to old recipes (Cennini, 2009). All paints were obtained by brushing the mixtures on canvas prepared with gypsum and rabbit glue, completely covering the canvas to obtain opaque samples with a mass tone as defined by Mayer (Mayer, 1991) and no varnishes were added.

The LA-TiO_2 NPs and SA-TiO_2 NPs CDs were applied on yellow and blue painting samples, respectively. The application is performed by brush in different time steps because of the slow water absorption by the painting. After the application of the self-cleaning solution, two

types of materials supposed as dirt were applied to both the samples. They are an organic carbon black pigment and Methylene-Blue (MB) dye used to test the photo-degradation at different exposition time intervals.

The methods

In order to evaluate the photocatalytic activity of laser ablated and commercial nanoparticles dispersed in water UV photo-degradation test with Methylene-Blue (MB) dye was carried out at different time steps. For these tests, 10 mg/l of MB for each milliliter of LA-TiO_2 NPs and SA-TiO_2 NPs CDs was added.

The UV irradiation is performed in a Color Assessment Cabinet of VeriVide using the UV Blacklight (368 nm) at 1.1 mW/cm^2. During the UV irradiation, the solutions were placed in quartz cuvettes with an opposite plug to avoid evaporation. The irradiation times were 30, 60 and 120 minutes for the colloidal dispersion and 60, 240, and 840 minutes for paintings. The degradation rate was measured after 30 minutes of irradiation to overcome the non-linearity effects due to MB degradation kinetics (Yogi, 2008).

The UV-VIS spectra are collected using Perkin Elmer Lambda 25 spectrometer with an accuracy of 0.1 nm.

The color measurements on colloidal dispersions are performed in transmission by using Konika Minolta CR5 colorimeter with di/180° (diffuse illumination/180° viewing) geometry. The D65 illuminant and the CIE 1964 standard colorimetric observer (10° standard observer) are used. The black (0%) and white (100%) adjustment scale was carried out with specific standards with which the instrument is equipped.

The spectrophotometric analysis on painting samples was conducted in reflection using a Konica Minolta® spectrophotometer, model CM-2600d with measurement geometry d/8°, selecting an area of 6 mm in diameter (SAV, Small Average Value). The results are related to the D65 illuminant and the CIE 1964 standard colorimetric observer (10° standard observer). The scale adjustment is an important step of the measurements (Gueli, 2019), and it was performed using the white calibration plate (CM-A145) as a target for the maximum lightness and the device CM-A32 for the minimum lightness. The data elaboration regarded SPEX/100 values (SPecular component EXcluded and UV included), were performed by dedicated software (SpectraMagic®), while Origin® software (OriginPro 8) was used for data processing.

By the spectrophotometer, we can study the Spectral Reflectance Factor (SRF%) trend in the visible range spectrum (400-700 nm) and we can calculate the color coordinates. We chose for the colorimetric examination the CIELAB 1976 space (Oleari, 2016), the most used in Cultural Heritage (EN1586:2010, Oleari, 2016, Gueli, 2017, 2018a, 2018b). This space describes mathematically all perceivable colors in the three dimensions, L* for lightness and a* and b* for respectively the color opponents green–red and blue-yellow coordinates.

In CIELAB, the color difference ΔE^*_{ab} is calculated as following (EN1586:2010, CIE15:2004):

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

where ΔL*, Δ*a**, and Δ*b** are calculated considering the painting with CDs before and after the UV irradiation.

Concerning ΔE^*_{ab}, values ranging from 0 to 1 were considered as not perceptible by human eye, for values between 1 and 2 only experienced observers can notice the color difference. ΔE^*_{ab} higher than 3.5 were considered as clearly visible (Mokrzycki, 2011).

All the data are elaborated considering the average values, resulting from five acquisition measurements, and the related uncertainties were calculated. The total uncertainties have been calculated according to the propagation uncertainties theory, as the square root of the squaring sum of standard deviation and instrumental error. This last contribution was estimated on the basis of CIELAB coordinates measured on white calibration plate.

In order to have qualitative information about elemental distribution, ion beam PIXE analysis has been performed with the external end-station of the AGLAE facility (Pichon, 2014) of the *Centre de Recherche et Restauration des Musée de France* (C2RMF) in the Louvre Museum in Paris. A 3 MeV proton beam was extracted through a 0.1 mm thick Si_3N_4 window (surface 1 mm^2) and delivered to the samples 5 mm downstream, with a magnetic focus allowing a beam spot about 50 mm wide. For PIXE analysis, three 50 mm^2 SDD detectors have been used with a 100 mm aluminum filter to enhance the detection of high energy X-rays, while one SDD with a smaller solid angle was used in a helium atmosphere to enhance the response to low energy X-rays.

Results and Discussion

First, the photocatalytic activity of LA-TiO_2 and SA-TiO_2 CD photo-degradation of MB and the UV-VIS absorption spectra are presented together with the CIELAB changes during the discoloration. After, the self-cleaning LA-TiO_2 and SA-TiO_2 CDs are applied on painting surfaces described in the Materials and Methods section. The optical behavior of the surfaces was investigated by SRF% trend in order to check the influence of the two types of colloidal dispersions on the colored surfaces and to verify the photo-degradation of two types of dirt selected in this work: organic carbon black pigment and Methylene-Blue dye.

Colloidal dispersion photocatalytic activity

The UV-VIS absorption was performed in order to characterize the CDs in water after the preparation. Figure 1 shows the spectrum of laser ablated titania nanoparticles in deionized water. An absorption around 400 nm is visible, at a longer wavelength the extinction is due to the scattering.

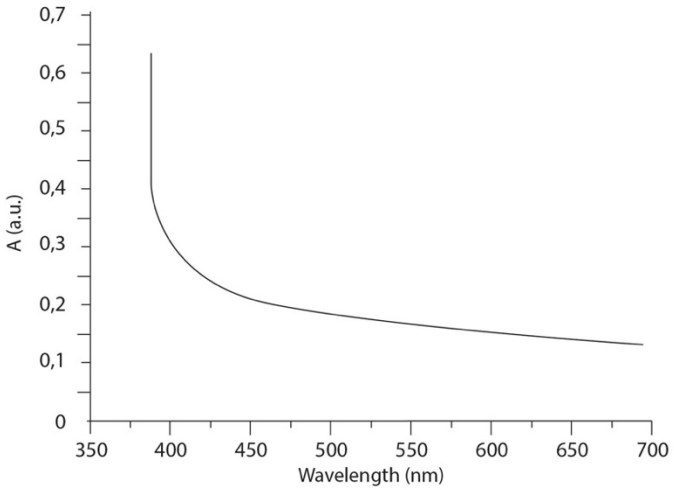

Figure 1 – Absorbance behavior of laser ablated titanium oxide nanoparticles

The photocatalytic activity of TiO_2 nanomaterials was measured by discoloration of MB dye. In Figure 2a, the absorption spectra of MB with LA-TiO_2 NPs CDs after UV irradiation for different time intervals are shown. The spectra are subtracted from the contribution of the reference represented by Milli-Q water. Using the absorption at 664 nm as a marker of MB concentration, we plotted in Figure 2b the MB concentration as a function of UV irradiation time.

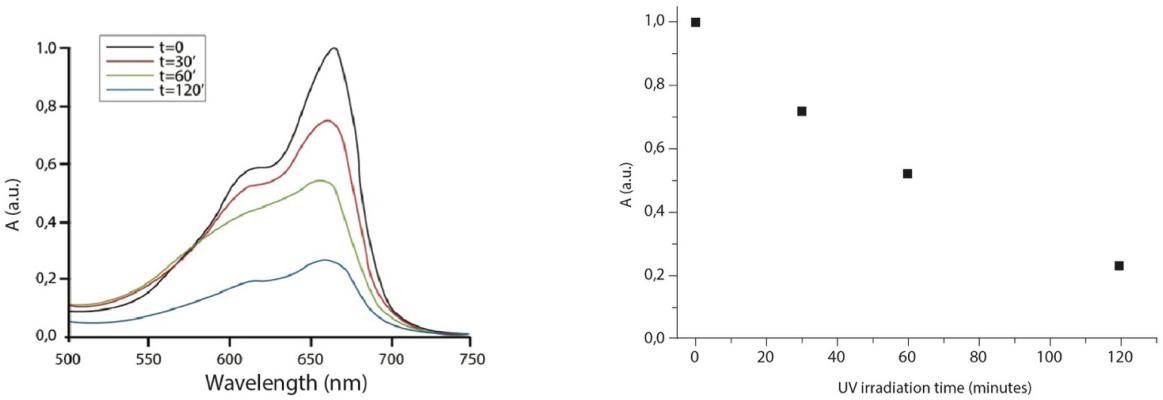

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Figure 2 – a) Absorption spectra of MB after UV irradiation for different times; b) MB absorbance at 664 nm as a function of UV irradiation time.

For characterizing the photo-degradation process from a colorimetric point of view, the transmittance measurement by a colorimeter was conducted. Table 1 shows the ΔL*, Δa*, Δb* values calculated between the colloidal dispersions obtained by LA-TiO_2 NPs and SA-TiO_2 NPs before and after the adding of MB in order to highlight the color changes of the CDs.

In the same table, the discoloration action by TiO_2 NPs is examined by the ΔL*, Δa*, Δb* values calculated before (@t=0) and after two different UV irradiation time intervals

Table 1 – The ΔL*, Δa*, Δb* values calculated considering the color coordinates with and without adding of MB for laser ablated and commercial nanoparticles and before (@t=0) and after two different UV irradiation time intervals (@t=120 minutes for LA-TiO_2 NPs and @t=60 minutes for SA-TiO_2 NPs). The uncertainties are calculated according to error propagation theory.

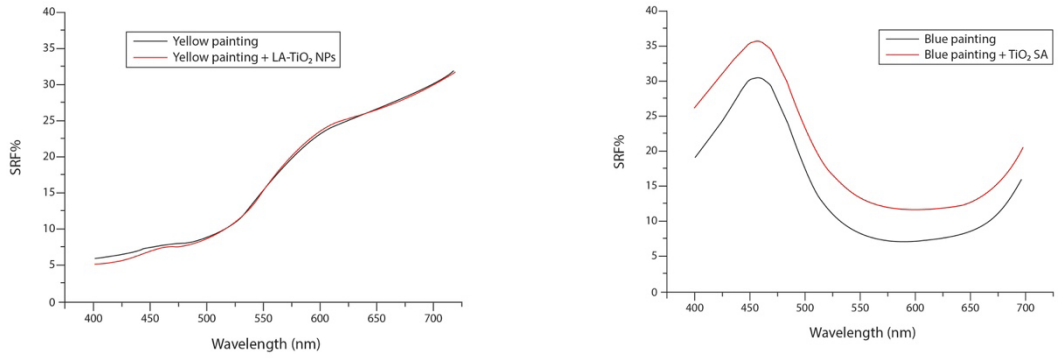
Colloidal dispersion	**ΔL*±δ**	**Δa*± δ**	**Δb*± δ**
LA-TiO_2 NPs + MB	-1,38±0,78	4,89±1,22	-4,35±1,21
SA-TiO_2 NPs+ MB	-23,94±1,13	-7,60±1,87	-24,53±1,36
LA-TiO_2 NPs + MB @t=120 min	-5,59±1,02	-6,77±1,65	5,20±1,11
SA-TiO_2 NPs + MB @t=60 min	8,47±1,76	7,72±1,64	21,31±1,34

The calculated color differences quantify the color changes to blue that is visible at naked eye caused by the addition of MB. The dye implies a darker blue-shift more marked for SA-TiO_2 NPs ΔL* and Δb*are equal to -23,94 and -24,53) than LA-TiO_2 NPs (ΔL* and Δb*values are equal to -1,38 and -4,35). About the discoloration of MB dye, the blue color shift is more evident for SA-TiO_2 NPs that in 60 min reach values of Δb*positive (21,31) greater than LA-TiO_2 NPs (5,20) in 120 min. These results could be imputable to different concentrations in the two CDs (Nam, 2019).

Photocatalytic activity on painting samples

After testing the photoactivity in water dispersion, the LA-TiO_2 NPs and SA-TiO_2 CDs are applied on yellow and blue painting samples and the photocatalytic activity is tested by SRF% trend study and by color changes in terms of DE^*_{ab} values.

In Figures 3 (a-b)**,** we show an example of the SRF% trends of LA-TiO_2 NPs and SA-TiO_2 CDs applied on yellow and blue paintings respectively. Only in the case of blue paintings, the SA-TiO_2 colloidal dispersion increases SRF% because of the white color of CDs. The color difference $DE^*_{ab,}$ calculated before and after the spreading of TiO_2 CDs on the yellow and blue paintings, are, in the case of LA-TiO_2 NPs, lower than 1, while, in the case of SA-$TiO_{2,}$ are more than 5. The DE^*_{ab} values confirm the difference between the two colloidal dispersion when they are applied on painting surfaces, especially in terms of lightness.



a b

Figure 3 – SRF% trends in function of wavelength in the visible range of yellow and blue paintings before and after LA-TiO_2 NPs application (a) and SA-TiO_2 NPs (b).

In order to test the self-cleaning action of LA-TiO_2 NPs CD, yellow paintings are stained with black carbon and MB and the samples are UV irradiated at different steps. After, spectrophotometric measurements were carried out to highlight the optical changes. In Figure 4, the comparison between SRF% trends for yellow paintings stained with black pigment and with (a) and without (b) LA-TiO_2 NPs CD is shown for different UV irradiation times. In particular, in Figure 4a it is possible to see an increase of SRF% that could be related to an increasing of lightness. This means, from a colorimetric point of view, that the surface is whiter due to the photocatalytic action of TiO_2 NPs.

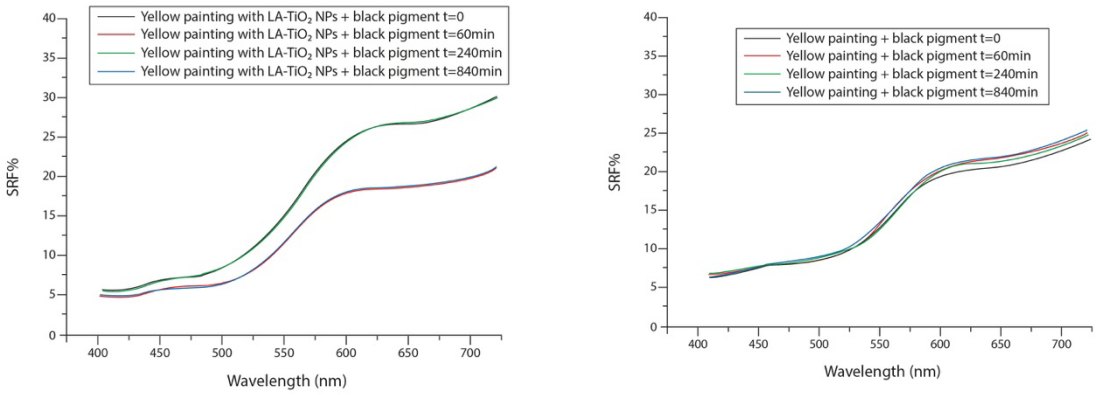


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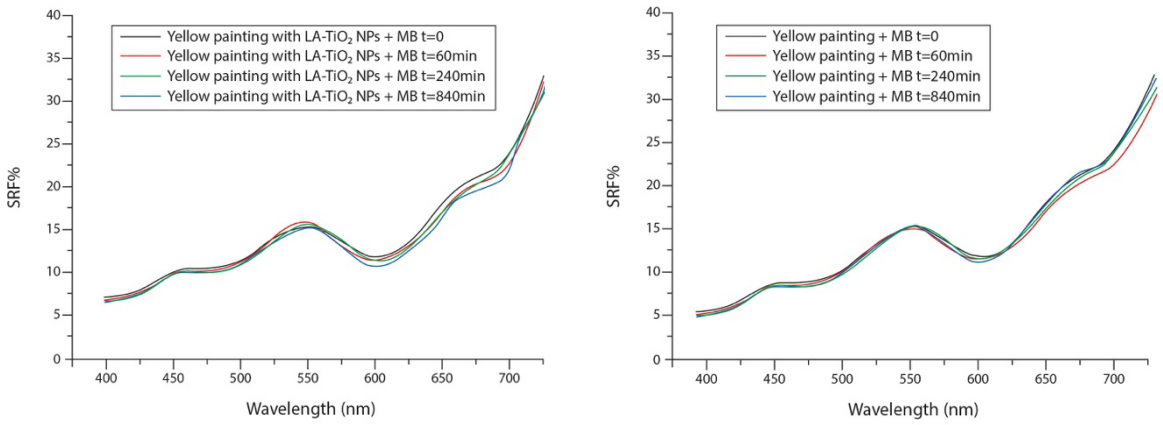
Figure 4 – Comparison between yellow paintings, stained with black pigment with (a) and without (b) LA-TiO_2 NPs CD) at different UV irradiation times.

The same procedure is replicated with MB dye and the result in terms of SRF% trends are reported in Figure 5(a-b). In this last case, the SRF% trend is homothetic in the two types of samples (with and without LA-TiO_2 NPs). This could depend on the nature of the materials

used to stain the paintings. The addition of MB to the yellow surface led to a change in green color, as visible in Figure 5 by the presence of the increasing of SRF% in the region about 500-550 nm. Furthermore, the MB dye can most deeply penetrate the painting and can react differently with the substrate respect to black carbon pigment.



a b

Figure 5 – SRF% trends of yellow painting after staining with MB dye and at different UV irradiation times with LA-TiO_2 NPs CD application (a) and without (b).

We tested also the commercial nanoparticles on blue painting samples and the SRF% behaviors are reported in Figure 6 showing that no significant changes in SRF% trends occur.

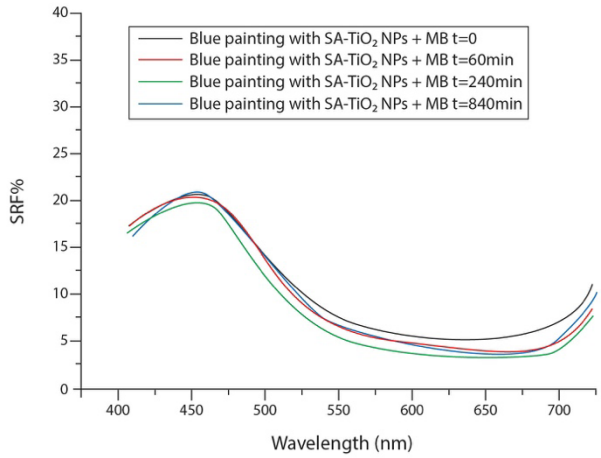
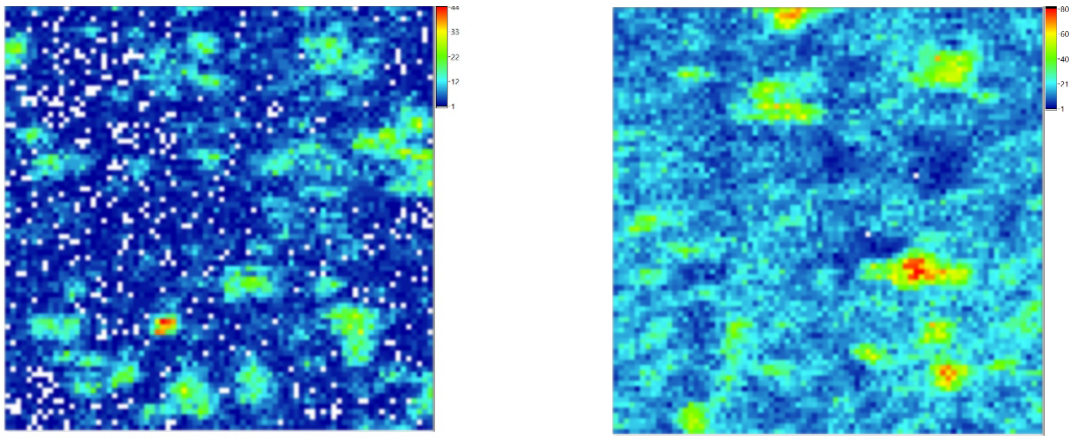


Figure 6 – Blue paintings with SA-TiO_2 NPs CD application and staining with MB dye at different UV irradiation times.

In order to acquire qualitative information about titanium distribution on the surface, we carried out PIXE maps. In Figure 7, the PIXE maps of LA-TiO_2 NPs yellow paintings (Figure 7a) and SA-TiO_2 NPs blue paintings (Figure 7b) are compared. The titanium seems to be

aggregated in clusters and localized only in small areas. The non-homogeneity titanium distribution could explain the failed photo-degradation (Pellegrino, 2017).



a b

Figure 7 – PIXE maps of (a) LA-TiO_2 NPs yellow paintings and (b) SA-TiO2 NPs blue paintings.

Conclusion

The aim of this contribution is to present a new research project aimed at assessing the use of titanium dioxide in painting conservation. In particular, we used TiO_2 colloidal dispersions obtained by a new and "green" methodology as the Pulsed Laser Ablation in Liquids. Firstly, the photocatalytic activity of laser ablated titanium dioxide nanoparticles is assessed by Methylene Blue dye discoloration method and compared with commercial TiO_2 nanoparticles using UV-VIS spectrophotometric technique and colorimetric measurements. After absorbance spectra characterization, the discoloration of MB dye is evaluated by colorimetry. The color changes are more evident for SA-TiO_2 NPs that in 60 min reach values of Δb* positive (21,31) greater than LA-TiO_2 NPs (5,20) in 120 min.

We tested the photocatalytic activity on painting. The samples are prepared in laboratory according to old recipes. For evaluating the efficiency in terms of cleaning performance of the TiO_2 based nanomaterials, the samples are stained with specific material and they are subjected to UV irradiation cycles at different times. The preliminary results about the feasibility assessment of the colloidal dispersions on paintings show that no significant photo-degradation is performed on the paintings towards the two materials (black carbon pigment and Methylene Blue) selected for testing the photocatalytic activity. The absence of TiO_2 photoactivity could be due to the inhomogeneity of the titanium distribution and to the formation of clusters on the paint surface as evidenced by PIXE technique. A new campaign of measurement is ongoing on a new set of painting samples improving the spreading of the colloidal dispersion.

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Authors' *Curriculum Vitae*

Stefania Pasquale is currently a Ph.D. student in Material Science and Nanotechnology at Catania University. She received a master degree in Sciences for Conservation and

Restoration of Cultural Heritage from Parma University in 2011. Her research interests are material science applied to cultural heritage.

Contact: stefania.pasquale@ct.infn.it

Vittorio Privitera is Research Director at the Italian National Council of Research (Institute of Microelectronics and Microsystems, CNR) and Section Head of the IMM Catania Unit. His current research is focused on the application of functional nanomaterials to water purification.

Contact: vittorio.privitera@imm.cnr.it.

Maria Miritello is a member of the research staff at the Institute for Microelectronics and Microsystems (IMM) within Consiglio Nazionale delle Ricerche (CNR) in Catania, Italy. Her research activity is mainly focused on the development of innovative materials for the realization of advanced devices for Si photonics, microelectronics and photovoltaics.

Contact: maria.miritello@ct.infn.it

Massimo Zimbone is a researcher of Consiglio Nazionale delle Ricerche (CNR) in Catania. His research activity is focused on material science and in particular on titanium oxides nanostructures, Silicon carbides and plasmonic nanoparticles.

Contact: Massimo.zimbone@ct.infn.it.

Politi Giuseppe is an associate professor of Experimental Physics at the University of Catania. His research interest, in the Cultural Heritage, field regards the application of Ion Beam and X-Ray Fluorescence techniques.

Contact: giuseppe.politi@ct.infn.it

Anna Maria Gueli is an associate professor of Applied Physics at the University of Catania and the Head of PH3DRA (*Physics for Dating Diagnostics Dosimetry Research and Applications*) laboratories. Her research and education activities mainly regard the application of color and imaging sciences in archaeometry and in health physics.

Contact: anna.gueli@ct.infn.it.

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