Analysis of the distribution of titanium oxide nanoparticles on paintings

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Abstract. This work is addressed to analyse the distribution of titanium dioxide nanoparticles on painting crossing data coming from two methodologies. Scanning Electron Microscope and Proton Induced X-Ray emission techniques have been employed in the study of the interaction between a colloidal dispersion constituted by titanium dioxide nanoparticles and the painting surface. The former e was used to understand and morphology of the painting and to investigate the distribution of the nanoparticles on the entire cross section of the pictorial layers. Proton induced X-ray emission is aimed at examining the surface titanium distribution by mapping.
This study is important because the exploitation of the photocatalytic activity of the titanium dioxide is possible only in the case of absorption of proper energy that can promote the oxide reduction reactions and thus the dirt and dust degradation.

1. Introduction

Over the last years, the interest in the production and use of new nanostructure materials in cultural heritage conservation has been growing. So far, the most used nanomaterials are oxides and hydroxides of alkaline earth metals because of their deacidifying properties combining with their ability to penetrate works of art and consolidate them [1-2]. The dispersions of calcium hydroxide nanoparticles have been used for restoration of lifted and flaking layers in wall-paintings [3-4] but also for deacidification of wood, paper and canvas.
In the last years, the titanium oxide self-cleaning efficiency has been tested on different materials belonging to cultural heritage with good results but never on paintings.
Still nowadays, paintings represent one of the biggest challenges because of their composite structure, constituted by both organic and inorganic materials and built up from the stratification of canvas and/or wood, ground, paint, and varnish layers. This complexity requires specific knowledge of the pictorial materials and the debate about the best cleaning and protective procedures is still open.
About the use of titanium dioxide on paintings different positions are discussed. It was proposed that titanium dioxide has both positive and negative influences on paint film durability. On one hand, adding titanium dioxide on a paint may improve its durability due to its protection and self-cleaning properties, on the other hand, it may negatively affect the paint due to the photocatalytic degradation of the organic components. According to some studies, titanium dioxide affects paintings' durability especially if it is used as pigment [5-6].
In this field, this research is addressed to investigate the possibility of use water-based colloidal dispersions prepared with titanium dioxide nanoparticles for self-cleaning and protective purposes. The titanium dioxide exposed to ultraviolet and/or to solar radiation can perform photocatalytic activity. This means that it may be able to increase the velocity of some chemical reactions and to degrade, by oxide-reduction reactions, many organic and inorganic substances [7]. For this reason, the titanium dioxide, applied on any material, can be used as self-cleaner as well as antimicrobic agent.
The use of nanoparticles can have important consequences for the self-cleaning of unwanted accumulated materials, such as dirt and dust that represent the first phase in deterioration, but also

varnishes and polymers left by previous restoration processes. The nanoparticles have been obtained by Pulsed Laser Ablation in Liquids and the water-based colloidal dispersions, exhibit optical characteristics suitable to be used in painting without altering the color properties of the surfaces [8-9]. To investigate the morphology of the painting surface and the distribution of the nanoparticles, the Scanning Electron Microscope (SEM) was used while the titanium distribution on the surface is mapped by the Proton Induced X-Ray Emission (PIXE).

2. Materials and Methods

2.1. Samples mock-ups

The research is performed on painting mock-ups prepared in laboratory according to old recipes, with historical pigments belonging to several chemical typologies and with historical binders (casein, egg yolk and linseed oil) [10]. The mock-ups are composed by a canvas substrate, a preparation layer of gypsum and by a paint layer obtained mixing, in a fixed ratio, pigments and binders according to protocol followed in previous research articles [11-12]. The dimension of each sample is 20 mm x 20 mm x 1 mm also including the substrate. Here the results related to the pigment Cadmium sulphide (CdS) is presented.

The water-based colloidal dispersion at concentration of 1mg/ml of titanium dioxide is applied by syringe to give the same quantity to wet each mock-up [13]. After the water evaporation, the nanoparticles can penetrate the strata of the painting and/or remain on the surface. The penetration and/or the distribution of the titanium dioxide must be verified.

2.2. Methods

Inverted trinocular microscope (OX.2253-PLF, Euromex) equipped with a 10X objective was used. The images were acquired with a sCMEX-20 camera (5440 x 3648 pixels, 20 MP, Pixel size 2.4 x 2.4 micron).

Two types of SEM microscope were used to observe the surface and the cross section of the painting mock-ups and to perform the elemental composition by EDX.

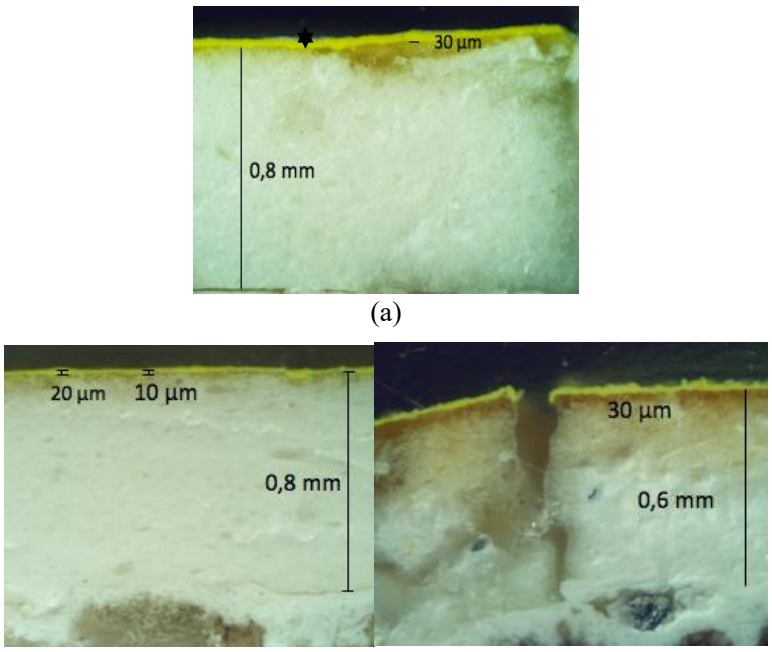
A Zeiss FEG-SEM Supra 25 microscope was employed to perform the plan view analyses. Images are obtained in the InLens detector that allows high efficiency collection of the Secondary Electrons (SE).

SEM-EDX analysis was performed using a SNE200M microscope equipped with a QUANTAX 100 Advanced BRUKER EDX microanalysis detector. The images were taken under low vacuum conditions on graphite-coated cross sections. The analytical conditions were 50X and 60X of magnification, 30 kV, and WD of 10 mm.

For PIXE analysis, a 3 MeV proton beam was extracted through a 0.1 μm thick Si3N4 window and delivered to the samples 2 mm downstream, with a magnetic focus allowing a beam spot about 50 μm wide. The spectra were collected with one SDD Low Energy X-ray (LE) detector and two SDD High Energy X-ray (HE) detectors, positioned respectively at 45° and 50° relative to the beam axis [14]. The LE detector, that had no filter, enabled the detection of light elements thanks to a helium flow reducing the absorption of low energy X-ray; on the other side, the high intensity of this component was reduced on the HE detectors by putting a 50 μm thick aluminium filter. PIXE data sorting and quantitative analysis is performed with TRAUPIXE AGLAE's software [15] using the GUPIX code [16], while by using the AGLAEMAP software it is possible to handle maps and pixel groups within maps, and by DATAIMAGING to display the resulting quantitative elemental maps [15].

3. Results and Discussion

In Figure 1, the cross sections of the paintings with casein (a), egg tempera (b) and linseed oil (c) are shown. The images highlight the paint layer has a thickness of about 30 μm and that this thickness is not always the same for all the surface while the preparation layer is about 0.8 mm. This is due to the homemade preparation realized with brush. Furthermore, in the case of linseed oil, for example, the surface presents craquelure and a minor thickness of preparation layer (0.6 mm) while in the case of egg tempera the paint layer is not homogeneously thick.

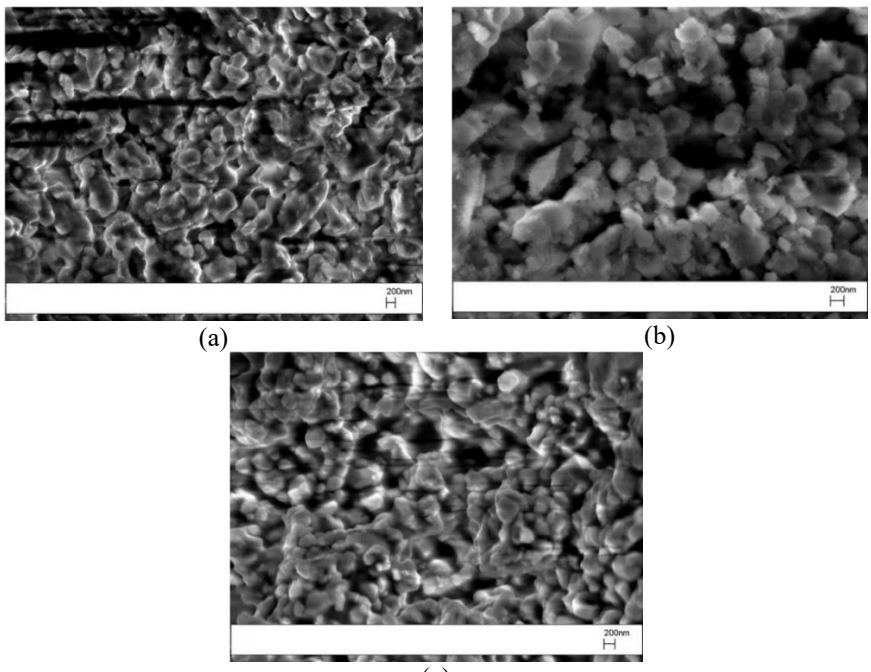


(a)

(b) (c)

Figure 1. Microscope image of the cross sections of painting realized with casein (a) and egg tempera (b) and linseed oil (c).

In Figure 2, the granular appearance of the painting surfaces is shown. In these types of topography, the determination of nanoparticles is challenging.



(a) (b)

(c)

Figure 2. SE-SEM images of painting prepared with casein (a), egg tempera (b) and linseed oil (c).

In Figure 3a, as example for the casein painting, the image acquired using backscattered electrons (BSE) of SEM is showed. With orange color the distribution of the titanium in the paint layers is highlighted. As visible, the titanium is on the surface of the Cadmium-based pictorial layer but the most quantity is penetrated in the interface between the preparation layer and the canvas. The image of Figure 3a underlines the point on which the EDX analyses were performed. In the EDX spectra (Figure 3c-d) the

titanium (Ti) is observed together with other elements. In the area 1 (Figure 3c), the Zinc (Zn), Si (Silicon), Sulphur (S) and the Cadmium (Cd) are detected. The Zinc and the Silicon are attributed to the preparation of the CdS pigment. In the point 2 (Figure 3d), also the Calcium (Ca), potassium (K), Silicon (Si), Sulphur (S), Magnesium (Mg) are detected, that are associated to the preparation layer.

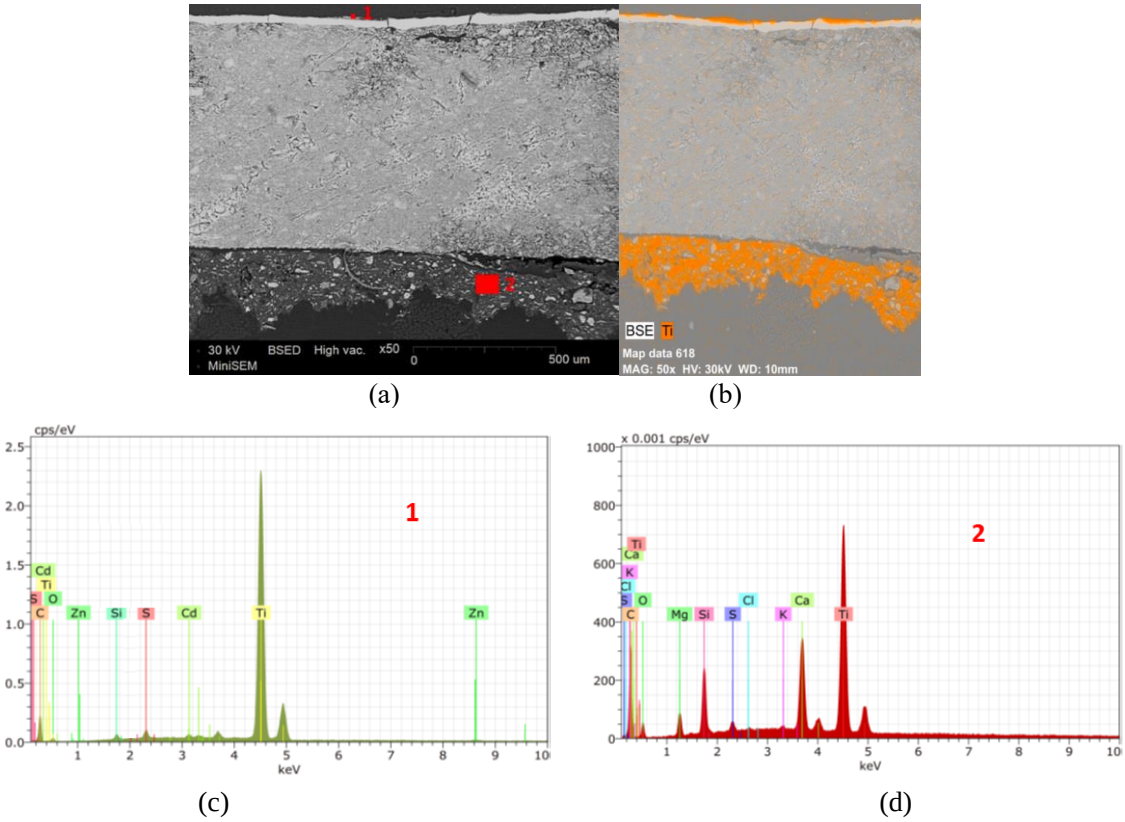


Figure 3. (a) BSE SEM images of the CdS + casein painting, (b) distribution of the titanium in the paint layer is highlighted in orange color. EDX spectra related to the 1 (c) and 2 (d) areas, indicated in (a).

To have qualitative information about titanium distribution on the surface of the painting, PIXE maps were acquired. In Figure 4, the PIXE map of a mock-up realized with linseed oil is shown. As it is possible to see, the distribution of titanium is not homogeneous.

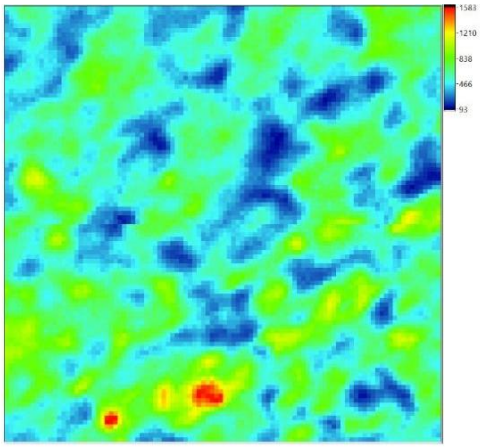


Figure 4. PIXE map of 2 mm^2 dimension of painting realized with linseed oil.

The analysis of the titanium distribution is important to understand the photocatalytic mechanism on the painting surface. It was necessary to assess the depth of ultraviolet radiation penetration through the paint layer, for a no diffusing layer or uniform composition material such as painting. This is not a trivial problem, and the mathematical treatment becomes a bit more complicated because painting not only absorbs radiation but scatters and transmits [17]. To take account all the phenomena, the Kubelka Munk model must be included in the calculation [18].
To have a preliminary estimation, in our case, the ultraviolet lamp, employed in the photocatalytic tests, maximum interact with some hundreds of micrometres [19]. This value agrees with literature data in which it was found that more porous structure of paint layer results in deeper penetration of ultraviolet radiation [20]. This means that the photocatalytic tests, conducted according to established procedures [21], give reliable results in terms of photodegradation of the dye used to simulate the dirt.

4. Conclusions

The use of the titanium dioxide nanoparticles in the painting surface for self-cleaning purpose is conditioned by the fact that the nanoparticles must absorb the proper ultraviolet energy necessary to active the oxido-reduction reactions. For this reason, it was important to characterize the painting surface and to detect the penetration of nanoparticles into the painting.
SEM and PIXE have been used to study the distribution of the nanoparticles on the entire cross sections and on the surface of painting mock-ups prepared in laboratory according to old recipes.
It was found that the nanoparticles penetrate the entire thickness of the paint layer (about 30 μm) until to the preparation layer. The morphology of the painting surface is granular and very inhomogeneous, and the determination of the nanoparticles is very challenging. The PIXE maps underline that the nanoparticles do not spread uniformly on the painting surfaces. All these information were useful to understand the mechanism of the photocatalysis of the titanium dioxide on painting for self-cleaning and protective purposes.

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