

# Deposition of Transparent, Hydrophobic TiO<sub>2</sub> Film for the Protection of Outdoor and Marine Cultural Heritage Assets

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In this work we present two new methods to obtain TiO<sub>2</sub> transparent coverage and to impart superhydrophobicity to stones and ceramics surface of monuments. The first method, adapted for small artifacts easily transportable in restoration laboratory, consists of a simple evaporation of Ti directly on ceramic surface in a controlled oxygen atmosphere. The second method consents the coverage of large surface directly *in situ*. The TiO<sub>2</sub> is evaporated on a salt surface with desired dimensions and then deposited on ceramic surfaces. In both cases the dioxide layers are transparent, don't damage the ceramic surfaces and are easily removable. In fact, the dioxide layer can be removed simply by 30 minutes of laser ablation process.

**Keywords:** Marine Artifacts; Photocatalic Activity; Protection of Cultural Heritage

## Introduction

In recent decades several scientific efforts have been made to fabricate superhydrophobic surfaces by using numerous techniques and methods, for example, plasma treatment (Manoudis, 2009; Chen, 1999; Coulson, 2000; Tserepi, 2006), photolithography (Oner, 2000; Gao, 2006) and sol-gel (Shirtcliffe, 2003; Mahltig, 2003; Hikita, 2005). Water repellent coatings can be important in many applications including, for example, the prevention of icing in cold weather, the promotion of self-cleaning process induced by rainwater on outdoor surfaces, the prevention of clotting in artificial blood vessels, the decrease of corona activity developed in conductors of transmission lines under rainy conditions, the production of waterproof and stain resistant textiles, and the reduction of friction in water (Manoudis, 2009; Gao, 2006; Zorba, 2008). One of the applications of the superhydrophobic coatings is their use as surface protective barriers for the preservations and conservation of ceramic and stone monuments. The most important degradation factor of outdoor, immovable cultural heritage is the rainwater which can causes stone deterioration through cycles of freezing and thawing inside the pores of the stones or by intraporous crystallization of the salts transferred by the water (Manoudis, 2009; Manoudis, 2008). For this reason, the application of hydrophobic coatings has been suggested for the surface protection of outdoor cultural heritage assets (Manoudis, 2009; Manoudis, 2008). Moreover several monuments are collocated in marine sites and cannot be removed from seabed, in these conditions the corrosion caused by marine water and microorganism can causes serious problems to conservation. Recently Manoudis et al. described (Manoudis, 2009; Manoudis, 2008) a

simple method that can be used to impart superhydrophobicity to different stones surfaces (used in restoration of the castle of Prague). This method is based on the dispersion of nanoparticle in a polymeric solution that can be sprayed on the substrate. The resulting composite polymer-nanoparticle film exhibits superhydrophobic properties.

However, this method cannot be applied in marine archeological sites (in underwater conditions the spray process is impossible and the dispersed particles can create environmental pollution). Moreover, in marine archeological sites the coverage of ceramic and stone must have an antibacterial action to inhibit the deterioration caused by the attack of marine microorganisms. In this optics, a surface coverage by TiO<sub>2</sub> substrate, with its photocatalytic oxidation properties (Liu, 2005; Naeem, 2010), can solve both the problems: idrophobicity and antibacterial activity.

Here we describe two simple methods to obtain TiO<sub>2</sub> coverage applicable in air and in marine water conditions. The obtained coverages are transparent (so it don't modify the artistic properties of monument) and hydrophobic, don't damage the ceramic surface and are easily removable by a simple cleaning process of laser ablation (Stranges, 2013).

## Materials and Methods

All the experiments were conducted on several ceramic fragments obtained from a "Carosello" (Gattuso, 2012), a structural hollow element made of clay, placed in arches, in domes or even and in the walls of buildings such as churches and houses, with the function lighten the structures (the specific "carosello" used in these experiments come from a site in Calabria: the Sanctuary of "Madonna del Buonconsiglio" in san Giacomo di Cerzeto, Cosenza, Italy dated back to 1844 ± 11). The frag-

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ments have dimensions of about 1 cm × 2 cm and a thickness of about 2 cm.

We implement two different TiO<sub>2</sub> coverage process. One, applicable to little fragments of ceramic artifacts, contemplates a titanium evaporation in ultra high vacuum chamber, while the second, applicable either in laboratory or in marine water, is a process of deposition of TiO<sub>2</sub> layer, previously evaporated on a salt, on ceramic surface.

The direct evaporation process was conducted in an ultra high vacuum chamber with a base pressure of  $1 \times 10^{-9}$  mbar. Ti was evaporated, in a controlled oxygen atmosphere (the partial pressure of oxygen in UHV chamber is fixed at  $5 \times 10^{-6}$  mbar), by heating an outgassed Mo boat filled with Ti crystal through a current of 60 A. The evaporation time ranged from 1 h to 7 h. The Titanium and oxygen atoms react on ceramic surfaces forming a TiO<sub>2</sub> layer (the formation of dioxide was confirmed by XPS data) with a thickness which increases with exposure time. **Figure 1** shows samples obtained with exposure times of 1, 2, 3 and 4 hours, the sample coloration is unchanged after 1 h of exposure while becomes darker with time evaporation, clearly indicating the formation of TiO<sub>2</sub> layers with a thickness greater than 30 nm (the dioxide coloration is strictly related to layer thickness and only for dimensions greater than 30 microns the layer is colored and visible to the naked eye).

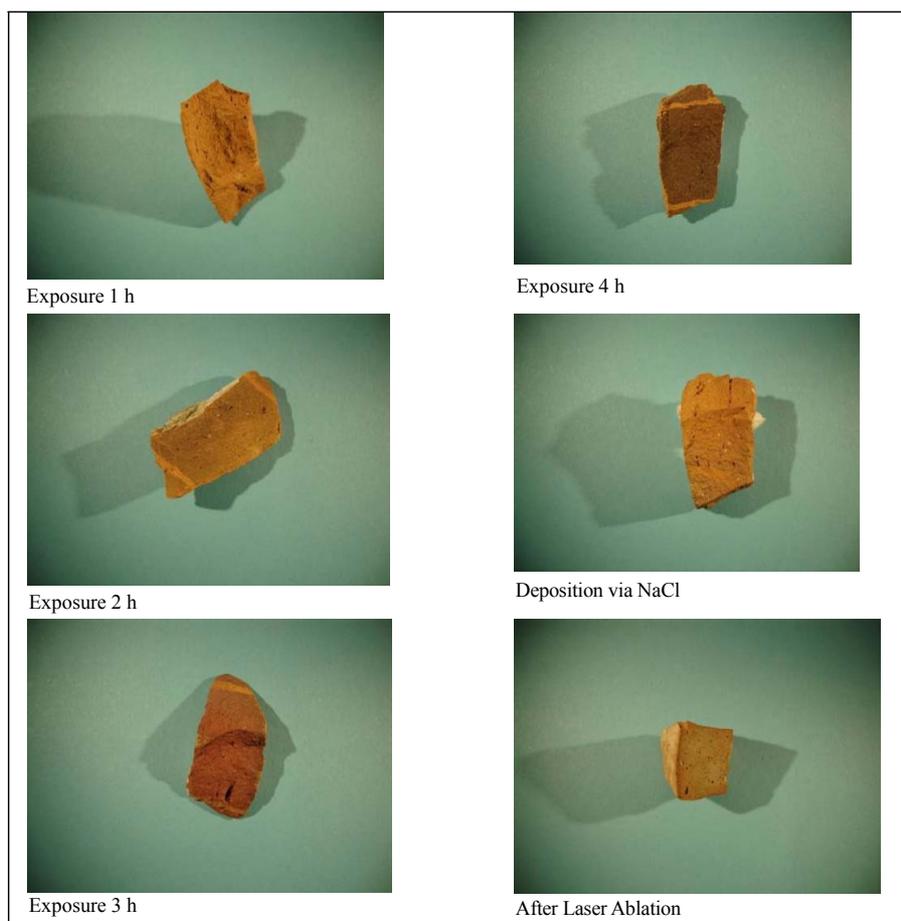
The deposition process includes two phases: a direct evapo-

ration on a water soluble salt surface (NaCl as example) using the process in UHV previous described and then the deposition of TiO<sub>2</sub> layer on ceramic surface on archeological site (air or marine water). The salt was deposited on Aluminum foil and then inserted in UHV chamber where an evaporation process of 1 h deposits a TiO<sub>2</sub> transparent layer. Following the TiO<sub>2</sub> layer is covered by a silicon adhesive layer (to favor the ceramic adhesion) and then sealed by aluminum foil to the application on ceramic. The salt surface and the aluminum foil were eliminated after deposition simply dissolving the salt with water. In this work we use as soluble salt the NaCl and the Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O obtaining the same results.

This process consent to prepare TiO<sub>2</sub> layer with desired dimensions in a laboratory and the application on ceramic surface directly *in situ*. **Figure 1** shows the ceramic covered by TiO<sub>2</sub> deposited via NaCl salt, the dioxide layer is transparent and not modifies the sample coloration.

All the TiO<sub>2</sub> covered sample are analyzed by X-ray photoelectron spectroscopy (XPS), X-ray fluorescence spectroscopy (XRF) and by contact angle measurements to testing the hydrophobicity properties.

XPS measurements were conducted in an ultra-high vacuum (UHV) chamber equipped for standard surface analysis with a pressure in the range of  $10^{-9}$  torr. Non monochromatic Mg-K $\alpha$  X-ray ( $h\nu = 1253.64$  eV) was used as excitation source. The



**Figure 1.** Images of “Carosello” fragments after Ti evaporation, after TiO<sub>2</sub> evaporation via NaCl and after laser ablation.

XPS spectra were calibrated with the C1s peak of a pure carbon sample (energy position 284.6 eV). All XPS spectra have been corrected by the analyzer transmission factor and background subtracted using the straight line subtraction mode. Moreover the XPS data were fitted assuming a Gaussian distribution.

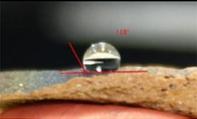
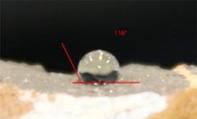
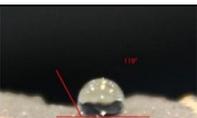
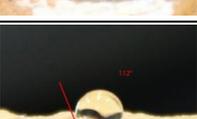
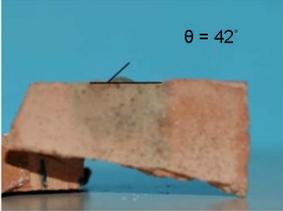
XRF measurements were conducted by the X-123 SDD apparatus by Amptek (USA), equipped by a gold cathode and a beryllium revelator, operating at fixed angle.

The contact angle images was obtained placing a small drop of distilled water (5  $\mu$ l) on the ceramic surface with and without dioxide coverage. The equilibrium contact angle was determined by drop shape analysis using an optical contact meter. The contact angle was measured several times for each sample to ensure data robustness.

After characterization all the samples was subjected to a Laser Ablation (LA) cleaning process to verify the reversibility of dioxide coverage and the possibility of future restoration on covered artifacts. The laser ablation procedure was performed irradiating for several minutes (15' or 30') each sample, immersed in an acetone solution, by the output of the first harmonic (1064 nm) of a Quanta-Giant series 710 Nd:YAG laser operating at 10 Hz. The spot size of the laser beam on the surface of carosello is about of (7 - 8) mm and the power of laser is fixed at 500 mJ/pulse. The immersion in acetone is necessary to prevent the oxidation and carbonization of surface induced by LA in air (Naeem, 2010). **Figure 1** shows the images of ablated artifacts, it is clear that the TiO<sub>2</sub> layer is completely removed as also confirmed by the results of XPS, XRF and contact angle measurements.

### Sample Analysis

The static water contact angle was analyzed to qualitatively assess the effectiveness of the surface coverage process and their influence on surface wetting. The sessile drop technique was employed. Indeed, the simple observation of a small liquid drop on a solid substrate provides useful information concerning the liquid-solid interaction and the hydrophobicity. The obtained results for both processes are summarized in **Figure 2**. The ceramic surface is completely hydrophilic and the water

TiO <sub>2</sub> directly evaporated on ceramic (evaporation times (h))	Contact angle $\Theta$ (°)	TiO <sub>2</sub> deposited with NaCl salt on ceramic	Contact angle $\Theta$ (°)
(7 h) 	118	 $\theta = 96^\circ$ After TiO <sub>2</sub> deposition	96
(6 h) 	116		
(5 h) 	119		
(4 h) 	112	 $\theta = 42^\circ$ After 15' LA	42
(3 h) 	111		
(2 h) 	107		
(1 h) 	110	 After 30' LA	0

**Figure 2.** Contact angle after all treatments described in paper.

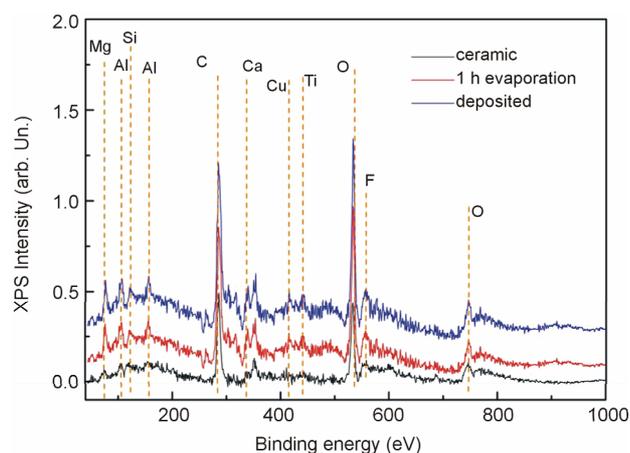
drop is completely adsorbed. These properties of ceramic is the origin of surface degradation in marine water or after exposure to atmospheric wet. So, the coverage with hydrophobic layer ensure the conservation of artifacts. However, the coverage must be transparent to not change the artistic and historic value of artifacts. For this we realize  $\text{TiO}_2$  coverage with different thickness (and different coloration) verifying the hydrophobicity for each obtained layer. **Figure 2** shows that the contact angle, and then the hydrophobicity, increases with evaporation time indicating for all samples an angle greater than  $90^\circ$  (hydrophobicity limit). In particular we obtain a contact angle of about  $110^\circ$  for transparent layer obtained by 1 h evaporation and an angle of  $96^\circ$  for transparent layer deposited via NaCl. These clearly indicate that in both process it is possible to obtain hydrophobic and transparent coverages.

LA process remove the  $\text{TiO}_2$  layer and the surface goes back to being hydrophilic. The contact angle, in fact, decreases to  $40^\circ$  after 15' of LA and until get to 0 after 30' of ablation. All these results was also confirmed by XRF and XPS analysis.

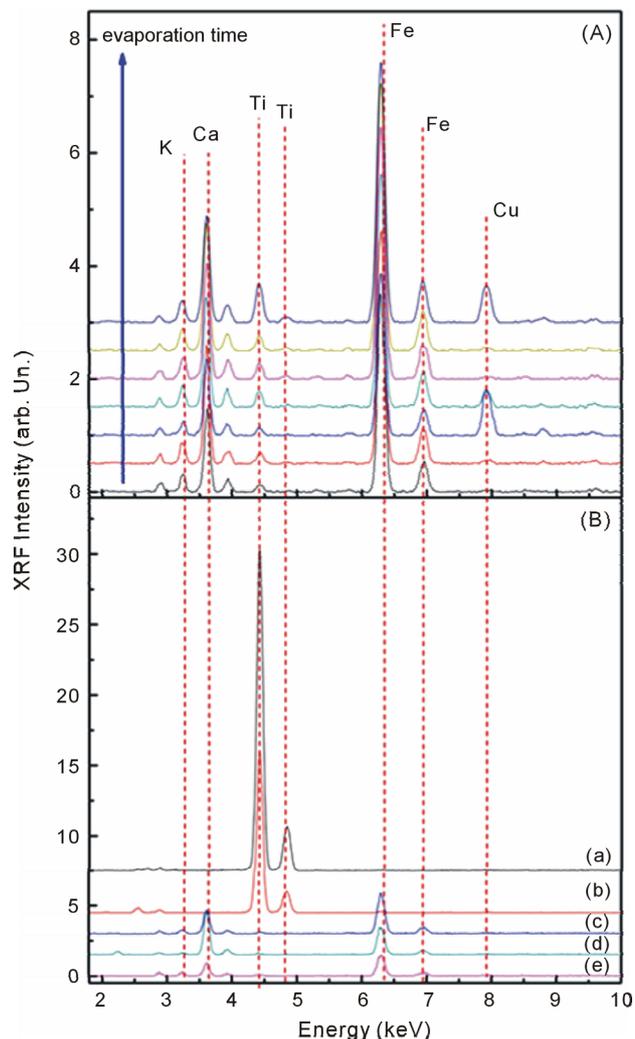
XPS data in **Figure 3** indicated that both process (direct evaporation and deposition) induce the only presence of Titanium and oxygen on ceramic sample without alter the sample composition or introducing impurities (Mo from evaporator boat, aluminum, sodium or chlorine from salt and deposition support foil). In particular in both process the Ti 2p lines are centered at 458.5 eV clearly indicated the only presence of  $\text{TiO}_2$  structures on surface (without presence of isolated Ti atoms) (NIST database).

XRF data in **Figure 4(A)** indicated that the amount of  $\text{TiO}_2$  increases with evaporation times indicating the formation of layer with thickness gradually larger. Data in **Figure 4(B)** indicates, moreover, the composition of deposited layer of  $\text{TiO}_2$  on salt (curve a for NaCl and b for  $\text{Na}_2\text{B}_4\text{O}_7$ ), it is clear that only  $\text{TiO}_2$  is present on salt surface without any presence of impurities. Curve c and d in **Figure 4(B)** indicates the surface composition after LA cleaning process (15' curve c and 30' curve d) it is clear that the Ti present on surface is completely removed and the sample spectrum is identical at this of pure ceramic (curve e).

Both process are, so, able to cover the ceramic surface giving to ceramic an hydrophobic characteristic which can protect the artifact from corrosion caused by marine water or atmospheric



**Figure 3.** XPS survey spectra for samples treated with different deposition process.



**Figure 4.** XRF spectra for sample s treated with different deposition process.

wet. The obtained substrate are moreover completely transparent and can be removed simply by laser ablation process without change the ceramic properties.

## Conclusion

In this work, we present two methods to cover ceramic artifact surfaces by a  $\text{TiO}_2$  transparent layer which gives surface to the properties of hydrophobicity which ensure a protection by water corrosion in marine water or in moist. The first process is a simple evaporation of Ti in a controlled oxygen atmosphere directly on ceramic surfaces. This process is applicable on small artifacts, and easily transportable in a restoration laboratory. The second method contemplates the evaporation of  $\text{TiO}_2$  on a salt surface (deposited on an aluminum foil) which can be successively deposited on artifacts. These methods prefer to the coverage of artifacts of different dimensions directly in situ, without damages of ceramics.

Both the process leads to the formation of transparent layer which don't damage the surfaces and don't introduce defects. Moreover the coverage is completely reversible. The dioxide layer can, in fact, be removed simply by a cleaning process of

laser ablation (30' at 1064 nm, 500 mJ) without surface damaging.

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