

Research Article

Marine Antifouling for Underwater Archaeological Sites: TiO_2 and Ag-Doped TiO_2

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Marine fouling plays a crucial role in the degradation of underwater archaeological sites. Limitation of fouling activity and its damages are one of the most critical issues for archaeologists and conservators. The common cleaning procedure, consisting in the manual removal of fouling, requires a continuous maintenance, while a proper inhibition of biological colonisation would provide a long-time protection against biofouling. On the other hand, the most used antifouling paints, especially for ship hulls, show considerable toxicity level. Since submerged archaeological sites are often included in environmental protected areas, more eco-friendly products must be used. We have explored the possibility to use titanium dioxide and Ag-doped titanium dioxide as antifouling agents. For this purpose, they have been synthesized by sol-gel method, and then XRD, XPS, and reflectance spectroscopy measurements have been carried out to gain structural information. The powders have been dispersed in a polymer and then applied to marble surface to evaluate the chromatic alteration induced by the treatments. By means of biological tests, it was possible to assess their behaviour as biofouling agents. Results show a decreasing of biofouling activity on treated stony surfaces.

1. Introduction

Biofouling plays a major role in degradation of submerged stone [1, 2]. This process develops within a few hours on material surfaces exposed to natural marine environments. At long exposure times, marine fouling occurs in the form of a complex community of plants, animals, and microorganisms that considerably alter and influence the immediate surroundings of the stone surface. Biofouling and biofilm formation are the result of an accumulation process, which is not necessarily uniform in time and space. On an active rough marble surface, the gelatinous structure of the biofilm (formed by extracellular polymeric materials “EPS,” bacterial cells, and water) is mixed with alteration products found on the stones that are formed within the same time scale [3]. The role played by microorganisms, both endolithic and epilithic

species, in the alteration of submerged stone materials is well known. This leads to the depletion and destruction of the substrate, by means of secretion of acids, surface deposits, and development of vegetative structures within the colonized stone. Research in this work has been focused on the experimentation of some innovative antifouling coatings suitable for stone materials. The antifouling coating technology has a long history, being studied since the 15th century [4]. Toxic antifoulants have been widely employed in the past as a method for controlling the fouling, but biocides such as lead, arsenic, mercury, and their organic derivatives have been banned due to the environmental risks associated with their use. A revolutionary self-polishing copolymer technique, using a similar heavy metal toxic action to deter marine organisms, consisted in the use of tributyltin- (TBT-) based antifoulant [5]. However, this latter caused shellfish

deformities and bioaccumulation of tin in some ducks, seals, and fish [6], resulting in legislations that culminated in the global ban of tributyltin [7, 8]. In the last decade, the scientific research has focused attention on alternative products, which have “acceptable” environmental impacts [9]. Nanometric oxides, such as TiO₂ and ZnO, are promising antimicrobial agents suitable for stone protection [10, 11] that act thanks to their photocatalytic effect [12–14]; in particular the anatase crystalline phase shows higher efficiency with respect to rutile [15].

The effectiveness of titania against marine antifouling has been studied only on glassy substrate [16]. Several papers have described the doping of titania with several elements [17–21] in order to enhance the bio- and photoactivity [22].

There are numerous studies on the properties and applications of Ag-TiO₂ systems used as photocatalysts, optical applications, and antibacterial treatment [23, 24].

Noble metals deposited or doped with TiO₂ have high Schottky barriers among the metals and thus act as electron traps, facilitating electron-hole separation and promoting the interfacial electron transfer process [25, 26]. Silver can trap the excited electrons from titanium dioxide and leave the holes for the degradation reaction of organic species. It also results in the extension of their wavelength response towards the visible region [27]. In addition, silver nanoparticles possess the ability to absorb visible light due to localized surface plasmon resonance (LSPR) [28]. These properties have led to tremendous range of applications of Ag-TiO₂ nanoparticles, for instance, antibacterial textiles, engineering materials, medical devices, food preparation surfaces, air conditioning filters, and coated sanitary wares.

In this work, we have synthesized titania and silver-doped titania and characterized them by means of XRD diffraction, reflectance spectroscopy, and XPS measurements. We have assessed the antifouling properties of these materials by performing microbiological tests. Finally we have dispersed such materials in a binder and applied them on marble specimens, and we have monitored the coating behavior in simulated marine environment.

2. Materials and Methods

Undoped TiO₂ was prepared using Ti(OBu)₄ as precursor. 5 mL of Ti(OBu)₄ were dissolved in 20 mL ethanol under ultrasonic stirring (20 minutes) and then 0.5 mL of HNO₃ solution (VHNO₃: VH₂O = 1:1), and 1 mL of H₂O were added dropwise to the above solution. The mixture was sonicated at room temperature for 30 min to obtain a white colloidal dispersion. The dispersion was dried at 100°C for 24 h and calcined at different temperatures for 6 h. The Ag-doped TiO₂ photocatalysts were prepared by the same procedure adopted for the pure TiO₂ except that an aqueous AgNO₃ solution was used instead of H₂O, and the Ag/TiO₂ ratio was 5% wt.

The X-ray diffraction (XRD) patterns of TiO₂ and doped TiO₂ were recorded on a D8 Advance Bruker X-ray diffractometer using Cu K α radiation as the X-ray source. The diffractograms were recorded in the 2θ range of 10–80°.

Measuring conditions were set at 40 kV voltage, 30 mA current, 0.02° 2θ step size, and 3.0 sec step time.

XPS measurements were conducted in a UHV chamber equipped for standard surface analysis with a base pressure in the range of low 10⁻⁹ torr. Nonmonochromatic Mg-K α X-ray ($h\nu = 1253.64$ eV) was used as excitation source. The XPS spectra were calibrated with the C1s peak of a pure carbon sample (binding energy 284.6 eV).

Photoluminescence (PL) and optical absorbance measurements were taken with an Olympus microscope (Horiba-Jobyn Yvon) mounting objectives of 10x, 50x, and 100x magnification. The microscope is equipped with a laser source at 378 nm (12 mW of power) for PL, a white lamp for absorbance measurements, and a Triax 320 (Horiba-Jobyn Yvon) spectrometer working in the 200–1500 nm range.

We measured directly the reflected spectrum ($I_r(\lambda)$) and obtained, by simply assuming the transmittance to be null for bulk samples, the reflectance ($r(\lambda)$) and the absorbance ($\varepsilon(\lambda)$) as a function of wavelength by the following relation:

$$r(\lambda) = \frac{I_r(\lambda)}{I_s(\lambda)} \quad (1)$$

$$\varepsilon(\lambda) = 1 - r(\lambda),$$

where $I_s(\lambda)$ is the source spectrum.

Marble probes (20 × 10 × 2 mm) were treated with a dispersion of TiO₂ (or Ag-TiO₂) dispersed in a binder (5% wt of acetone solution of Paraloid B72). As reference, untreated samples and samples treated with binder only have been also analysed.

Chromatic variations were assessed through colorimetric tests using a CM-2600d Konica Minolta spectrophotometer. Chromatic values were expressed in the CIE $L^*a^*b^*$ space, where L^* is the lightness/darkness coordinate, a^* the red/green coordinate ($+a^*$ indicating red and $-a^*$ green), and b^* the yellow/blue coordinate ($+b^*$ indicating yellow and $-b^*$ blue). The colour modification on the surface (ΔE) was calculated using the following relation [29]:

$$\Delta E = \left((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{1/2}, \quad (2)$$

where ΔL^* , Δa^* , and Δb^* represent the difference between the value of a specific chromatic coordinate in altered and fresh samples.

TiO₂, Ag, and Ag-doped TiO₂ were suspended in ultrapure water and sonicated for 10 min at 20% of power (Bandel electronic UV2070) and then sterilized in an autoclave.

To determine the efficiency of TiO₂ and its Ag derivate (Ag-TiO₂) without any interference of the organic components of the cultural media, experiments were carried out suspending separately two bacterial strains of the Bacterial Collection of the Department of Biological and Environmental Sciences at University of Messina. A Gram negative strain (*Stenotrophomonas maltophilia* BC 652) and a Gram positive strain (*Micrococcus* sp. BC 654) suspended in ultrapure (UP) sterile water were used.

Bacterial pellets were harvested by centrifugation at 10000 rpm per 10 min at 10°C and washed 3 times in UP

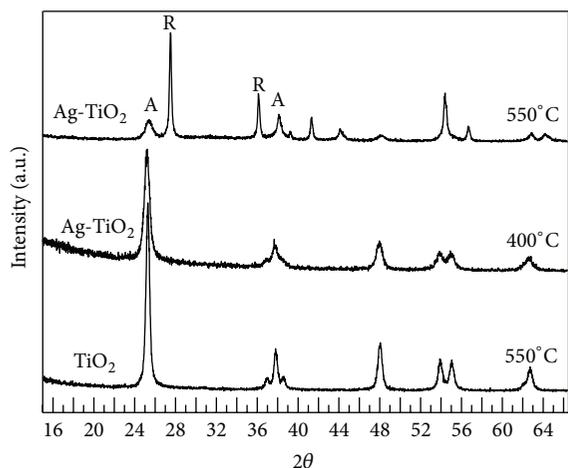


FIGURE 1: XRD patterns of titania and Ag-doped titania; A: anatase, R: rutile.

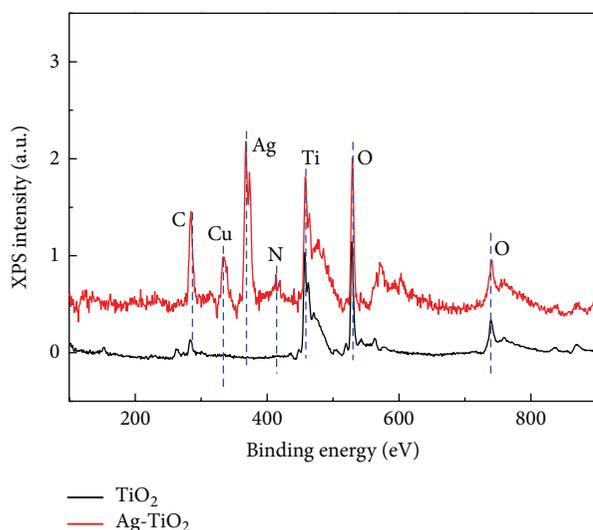


FIGURE 2: XPS survey recorded for titania and Ag-doped titania.

distilled water and then suspended to reach a final concentration of 1×10^6 cell/mL. They were inoculated in plates containing 0.1% and 0.01% (final concentration) of each product in double. Plates were incubated for 20 h under UV (UV 70030005/3V 25W Black) and solar lamp (Fluoradym R63 40 W).

The survival percentage was calculated after spreading on the surface of agarized medium (TSA, Oxoid) 100 μ L of each suspension and respective decimal dilution. After incubation at 28°C per 24–48 h, the percentage of survival was calculated as colony forming units per mL (cfu/mL).

Another test was carried out with marble slabs (treated and untreated) in simulated natural marine habitat. In this case, a simulation of submerged archeological artifacts was created in a container filled with marine water and a natural colonization of enriched marine bacteria was let to start and left for 24 h and for 72 h under natural daylight. Marble slabs were immersed in the marine water with an angle of 45° degrees in order to avoid bacterial passive sedimentation on

TABLE 1: XPS main line position and element amount (%) obtained from XPS data.

	Ti		O		Ag	
	Ti 2p (eV)	%	O 1s (eV)	%	Ag 3d (eV)	%
TiO ₂	458.3	27.8	529.9	72.19	—	—
Ag-TiO ₂	458.5	21.3	529.9	59.6	368.1	19.1

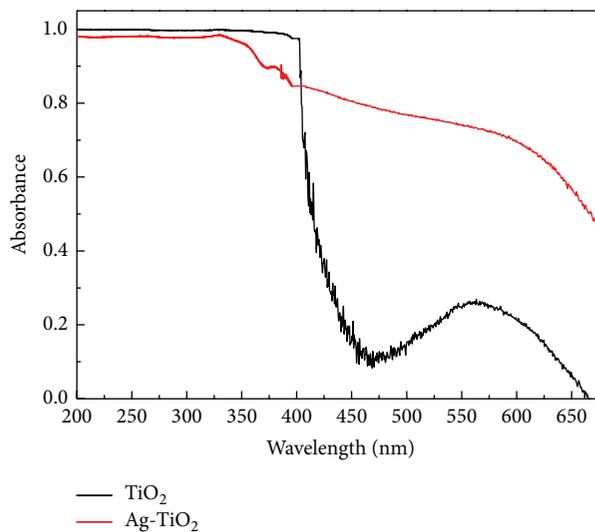


FIGURE 3: Reflectance spectra recorded for titania and Ag-doped titania.

the marble surface. Both upper part and lower part of marble slabs were analyzed.

After the incubation time, each marble slab was cut in two parts, one set fixed in Glutaraldehyde phosphate, dehydrated with a crescent series of alcohols (30-50-70-80-90-absolute), chrome metallized, and observed by SEM microscopy. For this purpose, an FEI Quanta 200F (Philips) scanning electronic microscope (SEM) has been used. All measurements were carried out with an acceleration voltage of 20 kV and under low vacuum conditions (10^{-5} mbar pressure).

3. Results and Discussion

In Figure 1, it has been shown the XRD pattern of titania and Ag-doped titania. It is worth to note that an annealing temperature of 550°C leads to the formation of anatase crystalline phase, while the presence of silver affects the crystallinity of the product, since a calcination temperature of 550°C leads to the formation of a mixture of anatase and rutile, while at 400°C only anatase is detected.

Information on the bonding nature and superficial composition are obtained with XPS analysis (Figure 2). Survey spectra indicate the presence of titanium, oxygen and silver, with traces of carbon and nitrogen probably adsorbed from atmosphere.

The main XPS lines for each elements are indicated in Table 1. Ti_{2p} and O_{1s} lines are characteristic of TiO₂ in all

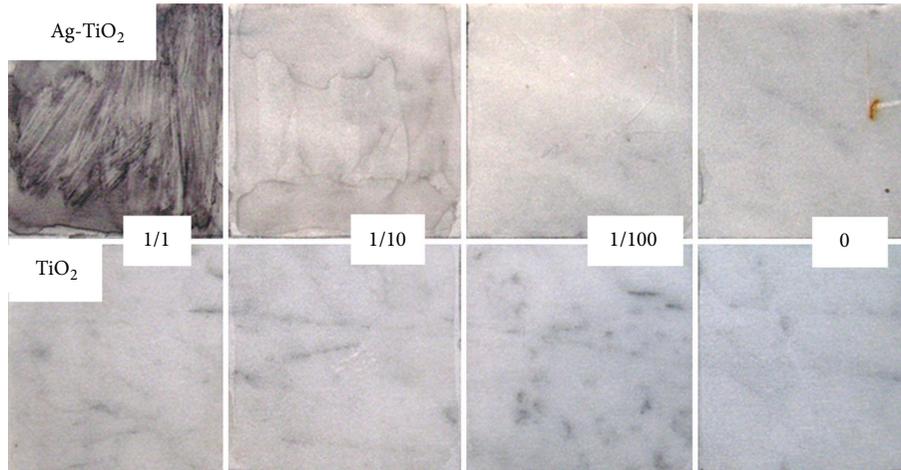


FIGURE 4: Treated samples with powder/binder mixtures at different ratios (1/1, 1/10, and 1/100).

samples, while the Ag 3d line is revealed, related to the corresponding oxide (AgO) indicating an oxidation of doping element caused by growing process [30].

These results indicate the absence of Ti-Ag chemical bond suggesting that interaction between TiO_2 and Ag has a van der Waals nature. Element's percentages, obtained from XPS data, indicate that Ag is strongly present on the surface layers of particles.

The optical absorbance, showed in Figure 3, changes strongly in visible region for doped samples. The absorbance of Ag-doped sample is about four time larger than pure TiO_2 . On the contrary, only little changes are visible in UV region.

The absorption of TiO_2 composite moved to longer wavelength in comparison with pure TiO_2 suggesting that the band gap was decreased by doping with Ag [31].

Synthesized powders were dispersed in different proportions (powder/polymer ratios: 1/1, 1/10, and 1/100) in Paraloid B72 solution in order to assess their suitability in terms of colour variations once applied to stony surface. Colorimetric measurements have been performed to assess chromatic variations induced by treatments (Figure 4); results are reported in Table 2.

Ag-doped titania provides strong colorimetric variations with respect to pure titania. The best compromise between aesthetic issue and product amount is represented by the 1/10 ratio, so this has been chosen as mixture to be applied on stone samples.

Results obtained from biological experiments showed that both bacterial strains were sensitive to the powders tested at a concentration of 0.1% and 0.01%. In particular, with TiO_2 tested at concentration of 0.1%, the percentage of survival cells was 55% and 19%, respectively, for *S. maltophilia* and for *Micrococcus* sp. (Figure 5), while the lower concentration of TiO_2 (0.01%) was more effective in determining the complete killing of bacteria tested. The doped TiO_2 with Ag determined a complete killing of bacteria at both concentrations; Ag alone was tested at the same concentration present in the doped TiO_2 gave comparable results.

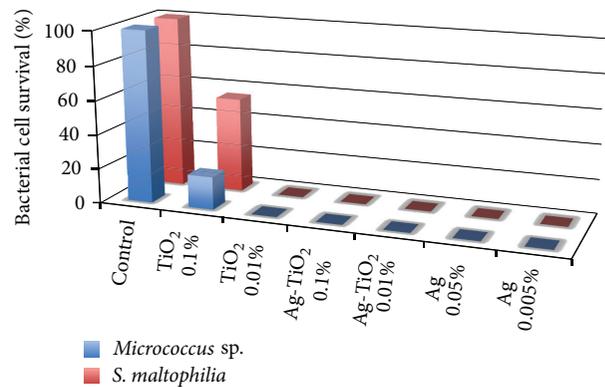


FIGURE 5: Histogram showing the percentage of survival cells in water of two bacterial strains tested against products under UV and solar lamp for 20 h. Controls were carried out with only bacteria.

Exposure of untreated and treated marble slabs showed a different response to the treatments after 24 h and 72 h of spontaneous colonization by microorganisms.

In fact, while the microbial colonization was irrelevant after 24 hours, after 72 h significant differences among the marble slabs were noticed (Figure 6). Untreated marble showed a higher production of EPS on the surface, while on the marble treated with the binder alone the surface was covered by occasional or no patches of EPS. Marbles treated with TiO_2 or Ag- TiO_2 or Ag alone showed no EPS production and no microbial colonization.

Our results showed that treatments with titanium oxides and their Ag derivate were very effective to control bacteria population, the process of adhesion, and consequent extracellular polymeric substances (EPS) formation. The results obtained were also comparable with the action of Ag alone.

However, due to the different sets of the experiments used, we can draw some conclusions.

In fact, in the first set of experiments carried out to test the survival of bacterial cells we could state that the photocatalytic effects of the tested products under laboratory

TABLE 2: Colorimetric measurement of treated and untreated surfaces.

Titania/binder	1/1			1/10			1/100			0			ΔE Treated-untreated		
	L^*	a^*	b^*	ΔE (1/1)	ΔE (1/10)	ΔE (1/100)									
TiO ₂	77.87	-0.55	0.17	78.95	-0.96	-0.55	79.11	-1.00	-1.24	80.82	0.80	1.62	3.55	3.36	3.79
Ag-TiO ₂	58.03	1.69	1.77	78.44	0.54	-0.46	80.44	-0.82	-0.19	82.98	-0.81	1.46	25.08	4.94	3.03

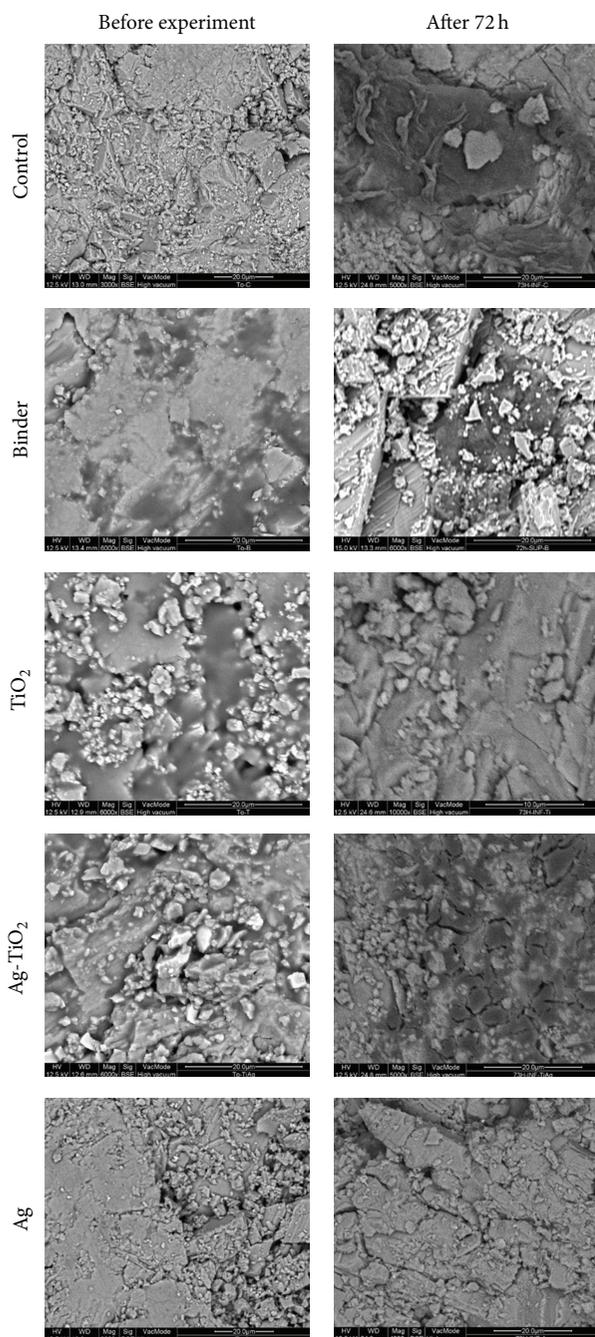


FIGURE 6: SEM pictures of the untreated and treated marble slabs before and after 72 hours of immersion in sea water simulation.

conditions were effective reducing dramatically the number of viable cells. However, this method suffers from limitation due to the fact that in field experiments the application of

products on the treated surfaces is necessary through the use of a binder and thus testing products alone is not comparable to the experiments in field conditions.

The other set of experiments, carried out with untreated or treated submerged marble slabs, showed that the products tested were effective against the first steps of colonization that is the main cause of the progression of biofouling of submerged surfaces. In fact, our experiments were successful because no EPS or bacteria colonization was observed after 24 h and 72 hrs of immersion of marble slabs treated with the products. On the contrary, control surfaces (untreated marble) showed the presence of EPS produced by the bacteria underneath (Figure 6).

4. Conclusions

This work has dealt with the synthesis, structural characterization, and biological assessment of pure and Ag-doped titania in order to explore the possibility to use them as antifouling agent suitable for the protection of submerged archeological stone artefacts.

A treatment, with a mixture of Ag-TiO₂/binder ratio of 1/10, represents the limit that should not be exceeded to avoid aesthetical issues on the stone surface.

As far as the antimicrobial tests were concerned, the goal of this study was to test a reliable standard method for testing the antimicrobial efficacy of TiO₂ photocatalytic products that could work on submerged objects. To achieve this objective, we used two methods that gave us promising results. The first method of determining the survival curve of tested bacteria gave us information on the sensitivity of bacterial strains. In this condition, bacterial sensitivity could be tested at different concentrations. The second method seems to be more promising but still some adjustments especially regarding the proper time of exposure are needed.

Although these results have a preliminary nature, it can be stated that a decreasing of biofouling activity has been observed on treated stony surfaces.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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