



ZrO₂-doped ZnO-PDMS nanocomposites as protective coatings for the stone materials

Maduka L. Weththimuni¹, Marwa Ben Chobba², Ilenia Tredici³, Maurizio Licchelli^{1,3}

¹ Department of Chemistry, University of Pavia, via T. Taramelli 12, I-27100, Pavia, Italy

² National School of Engineering, University of Sfax, Box 1173, 3038 Sfax, Tunisia

³ CISRiC, University of Pavia, via A. Ferrata 3, I-27100, Pavia, Italy

ABSTRACT

ZnO is a semiconductor that has found wide application in the optics and electronics areas. Moreover, it is widely used in different technological areas due to its beneficial qualities (high chemical stability, non-toxicity, high photo-reactivity, and cheapness). Based on its antibacterial activity, recently it has found also application to prevent bio-deterioration of cultural heritage buildings. As many authors suggested, doped ZnO nano-structures exhibit better antibacterial properties than undoped analogues. In the present work, ZnO nanoparticles doped with ZrO₂ have been prepared by a sol-gel method in order to enhance the photocatalytic properties as well as the antibacterial activity of ZnO. Then, ZrO₂-ZnO-PDMS nanocomposite (PDMS, polydimethylsiloxane used as the binder) was synthesized by in-situ reaction. The resulting nanocomposite has been investigated as a possible protective material for cultural heritage building substrates. The performances of newly prepared coating were evaluated on three different stones (Lecce stone, Carrara Marble and Brick) and compared with Plain PDMS as a reference coating.

Section: RESEARCH PAPER

Keywords: ZrO₂-doped ZnO; Nanocomposites; Protective coating; Self-cleaning effect

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Corresponding author: Maduka L. Weththimuni, e-mail: madukalankani.weththimuni@unipv.it

1. INTRODUCTION

Our artifacts provide the most important and essential availability for the culture of all countries and represent the symbol of history. Therefore, protection and conservation of this patrimony are essential tasks for the scientific community. The cultural heritage buildings undergo different damages, particularly because they are exposed outdoors, and are subject to a number of phenomena such as air pollution, water absorption, salt crystallization, photodegradation, and microorganisms colonization which cause transformation and deterioration of surfaces [1]-[3]. Moreover, decay of stone materials is strongly related to their porosity properties, which implies that highly porous materials often undergo faster degradation than the other stone substrates [4]-[6].

Several methodologies have been developed to clean preserved materials belonging to heritage sites as a first step of the conservation process. Cleaning procedures may include the use of solvents, chelating agents, and even of acidic or basic

agents [7]. Nevertheless, the irreversibility of these methods, the risk of altering the artwork, as well as the toxicity of certain products makes these cleaning procedures scarcely suitable for the application for historic buildings [7]. The bio-cleaning method has been suggested and studied as an alternative technique by using selected microorganisms [8]. Despite the efficiency of this method under the laboratory condition, the need of specified conditions to ensure the viability of these microorganisms make its practical application very difficult and subject to further studies [7]. Laser method has been considered as a friendly technique for cleaning heritage structure as well as for environment [9]. However, the high cost of this method is still the barrier against its widespread use. A variety of products (biopolymers, ionic liquids, gels, microemulsions, etc.) have been also proposed and used in this field, although their application still has some drawbacks such as high cost of maintenance and toxicological risks [10], [11].

The conservation of monumental cultural heritage with innovative nanocomposites is in the vanguard of conservation science and a plethora of research activities are dedicated to the

design and validation of compatible nanomaterials that may exhibit strengthening, hydrophobic and self-cleaning properties [12-14]. Moreover, scientists have focused their research to find out self-cleaning protective materials in order to reduce maintenance costs. In particular, titanium dioxide (TiO_2) and zinc oxide (ZnO) nanoparticles (NPs) have been studied and tested for self-cleaning applications [15], [16]. The interest in developing and using these nanosized materials in combination with different binders has increased due to their excellent self-cleaning and antibacterial properties in addition to their easy, non-toxic and non-expensive procedures of application [17], [18]. However, their technological application has some important limitations among which the easy recombination of charge carriers and the need of ultraviolet (UV) radiation as an excitation source, considered as the most restrictive drawback, are due to the broadband-gap (ZnO : 3.2 eV; TiO_2 : 3.3 eV for anatase) of the two oxides [19]. This limitation is particularly restrictive, as UV radiation corresponds to only 3 % of the solar irradiance at the surface of Earth. Therefore, many research groups have focused their efforts on enhancing the photocatalytic as well as the antimicrobial activity of pure NPs by doping with different ions (transition, non-transition, and non-metal ions) [1]-[20]. The process of doping can alter the surface reactivity, functionality and charge of the NPs, with possible improvement of their properties such as durability, stability, and dispersive ability of core material [20]. Some authors also reported that the doped nanostructures exhibit better antibacterial properties than undoped analogues [20]. Zirconium dioxide or Zirconia (ZrO_2) is a wide band gap P-type semiconductor, which is used in many fields due to its excellent properties (e.g. good natural color, high strength, high toughness, high chemical stability, and chemical and microbial resistance) [21].

The main objective of this work was the preparation of ZnO nanoparticles doped with ZrO_2 by a sol-gel method in order to enhance the photocatalytic properties as well as the antibacterial activity of plain ZnO . Moreover, doped NPs were combined with a binder (polydimethylsiloxane, PDMS) to obtain a nanocomposite, which was tested as a protective material for the Cultural Heritage.

At first, the synthesised core-shell (ZrO_2 - ZnO) NPs were characterised by SEM-EDS. After that, the performances of the nanocomposite coating (ZrO_2 - ZnO -PDMS) as a protective material for stone substrates were evaluated when applied on three different stone types: Lecce stone (LS), Brick (B) and Carrara Marble (M). Moreover, PDMS-treated stone specimens were used as the reference for each and every analyses. The evaluation of coatings was done by different techniques: contact angles and chromatic variation measurements, capillary absorption and water vapor permeability determinations, optical microscopy (visible and UV light), SEM-EDS, self-cleaning and antibacterial tests.

2. MATERIALS AND METHODS

2.1 Materials

Analytical grade sodium hydroxide (NaOH), ethanol (absolute, 99.8 % EtOH), zinc acetate dihydrate ($\text{ZnC}_4\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$), 2-propanol, zirconium oxychloride octahydrate, orthophosphoric acid, hexamethyldisiloxane, and octamethylcyclotetrasiloxane (D4, utilized as PDMS precursor) were purchased from Sigma-Aldrich. Cesium hydroxide ($\text{CsOH} \cdot \text{H}_2\text{O}$) was purchased from Alfa Aesar. All the chemicals

used without further purification. Water was purified using a Millipore Organex system ($R \geq 18 \text{ M cm}$). Lecce stone specimens (open porosity > 30 %) were provided by Tarantino and Lotriglia (Nardò, Lecce, Italy), while specimens of Brick (open porosity ~24 %) and Carrara Marble (open porosity ~0.5 %) were provided by Favret Mosaici S.a.s. (Pietrasanta, Lucca, Italy).

2.2 Preparation, application and testing methods of the nanocomposite

Before treatment, Lecce stone (LS), Brick (B), and Marble (M) (squared $5 \times 5 \times 1$ and $5 \times 5 \times 2 \text{ cm}^3$) specimens were smoothed with abrasive, carbide paper (No: 180 mesh), washed with deionized water, dried in an oven at 60 °C and stored in a desiccator to reach room temperature, then their dry weight was measured [2], [4].

First of all, ZrO_2 - ZnO core-shell NPs (molar ratio about 0.01:1 ZrO_2/ZnO) were synthesised by sol-gel method as reported in the literature [20], [21] and then, ZrO_2 - ZnO -PDMS nanocomposite was synthesised by in-situ reaction. For this purpose, doped NPs (0.5 % (w/w)) were introduced to the reaction mixture containing octamethylcyclotetrasiloxane (D4, 25 g) and CsOH (0.15 g), used as a catalyst for the ring opening polymerization of D4. After ultrasonication (20 minutes), the reaction was carried out at $120 \pm 3 \text{ }^\circ\text{C}$ under vigorous stirring for 2.5 hours in an oil bath and then, hexamethyldisiloxane (0.03 g) was added and the reaction was continued at the same temperature another 2.5 hours as recommended in the literature [20].

All the samples (LS, B, and M) were saturated with ethanol by keeping specimens at least 6 hours in absolute EtOH in order to prevent the penetration of coating inside the pores and ensure that it remains on the surface of the stone [1]. After saturation, all specimens were treated with ZrO_2 - ZnO -PDMS nanocomposite as well as with plain PDMS (as the reference) by brushing method (applied amount, $1.0 \pm 0.02 \text{ g}$ for each specimen). Specimen treated with the nanocomposite were named $\text{Zn-Zr-PDMS}_{\text{LS}}$, $\text{Zn-Zr-PDMS}_{\text{B}}$, and $\text{Zn-Zr-PDMS}_{\text{M}}$, while reference specimens were labeled PDMS_{LS} , PDMS_{B} , and PDMS_{M} .

Optical microscopy observations of the treated specimens were done using a light polarized microscope Olympus BX51TF, equipped with the Olympus TH4-200 lamp (visible light) and the Olympus U-RFL-T (UV light). Scanning electron microscopy (SEM) images (backscattered electron) and energy-dispersive X-ray spectra (EDS) were collected by using a Tescan FE-SEM, MIRA XMU series, equipped with a Schottky field emission source, operating in both low and high vacuum, and located at the Arvedi Laboratory, CISRiC, University of Pavia. The amount of absorbed water as a function of time was determined in accordance with the UNI EN 15801 protocol [22]. Water vapor permeability was determined according to UNI EN 15803:2010 protocol [23]. Color changes were measured by a Konica Minolta CM-2600D spectrophotometer, determining the L^* , a^* , and b^* coordinates of the CIELAB space, and the global chromatic variations, expressed as ΔE^* according to the UNI EN 15886 protocol [24]. Self-Cleaning efficiency of prepared coatings was performed by using MULTIRAYS, photochemical reactor, composed of UV chamber equipped with 8 UV lamps. The power of each lamp is 15W with a total power of 120 W. The reactor is equipped with a rotating disc in order to ensure a homogenized irradiation on all stained samples. The discoloration of methylene blue (MB) dye (0.1 % wt in ethanol solution), applied on the surface of treated stones specimens and

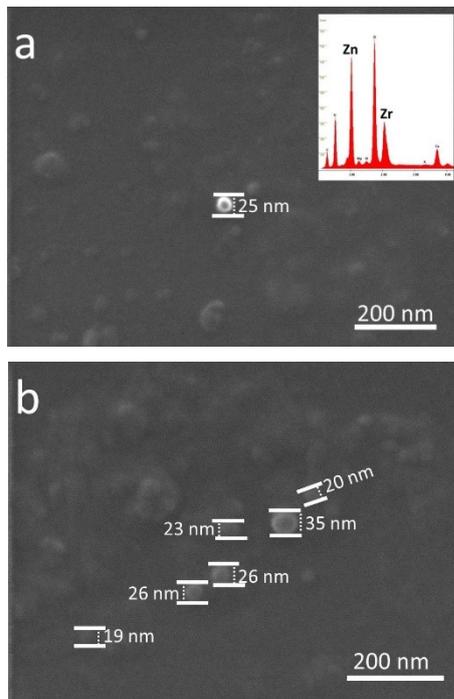


Figure 1. SEM images of doped NPs.

their untreated counterparts, was controlled by measuring chromatic variations (five control points for each sample surface) before and after application of MB dye, after 48 and 96 h of UV exposure. Discoloration parameter D^* was determined by using (1) [25]:

$$D^* = \frac{|b^*(t) - b^*(MB)|}{|b^*(MB) - b^*(0)|} \cdot 100 \% \quad (1)$$

where $b^*(0)$ is the value of chromatic coordinate b^* before staining, while $b^*(MB)$, and $b^*(t)$ are the mean values after the application of methylene blue over the surfaces and after t hours of UV-A light exposure, respectively. Here, b^* coordinate was considered, because this parameter is sensitive to blue colour.

3. RESULTS AND DISCUSSIONS

3.1 Characterisation of doped NPs and treated stone specimens

SEM-EDS analyses showed that ZrO_2 -doped ZnO NPs are homogeneously dispersed in the PDMS binder. Most of them are spherical with a size in the 15-30 nm range. Anyway, some particles displaying larger size and more irregular shape can be observed, which can be due to occasional aggregation (see Figure 1a-b).

EDS analyses performed on single particles showed the presence of both zirconium and zinc, confirming the expected elemental compositions of the doped inorganic NPs (Figure 1a).

Optical microscopy observations suggested that nanocomposite material (ZrO_2 -ZnO-PDMS) is homogeneously distributed on the treated stone surfaces (LS, B, and M). Moreover, it seems that the coating covered pores on the surface and acting as a protective layer to the stone (Figure 2). This observation was confirmed even by SEM experiments (Figure 3).

Quite acceptable chromatic variations ($\Delta E^* < 5$) were observed (see Table 1) after application of ZrO_2 -ZnO-PDMS on any considered substrate, suggesting that the natural colour of the stones is not dramatically affected by the treatment. The corresponding chromatic coordinates are graphically resumed in

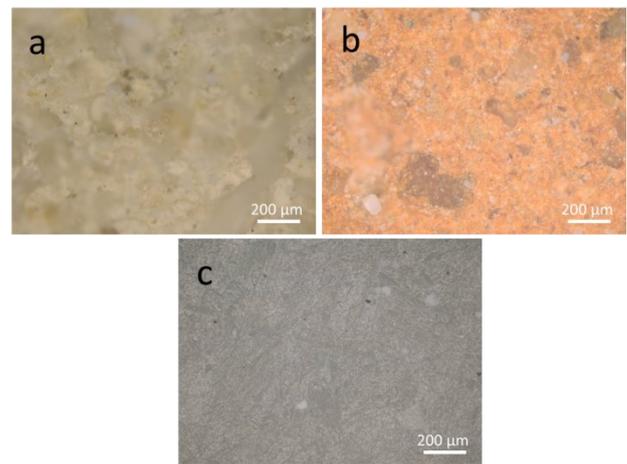


Figure 2. Optical microscope images of treated stones: (a) Zn-Zr-PDMS_LS, (b) Zn-Zr-PDMS_B, and (c) Zn-Zr-PDMS_M.

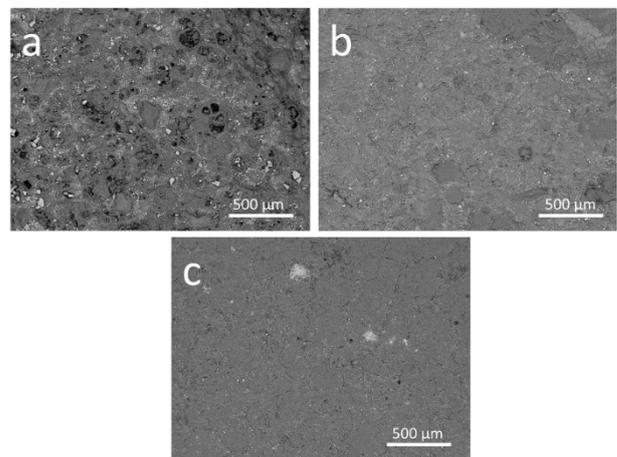


Figure 3. SEM images of treated stones: (a) Zn-Zr-PDMS_LS, (b) Zn-Zr-PDMS_B, and (c) Zn-Zr-PDMS_M.

Figure 4. Coordinate L^* (related to the lightness) is considerably affected by all the treatments, regardless of the considered treatment. Variations of b^* (related to the blue to yellow change) are more relevant on Lecce stone and Brick specimens treated with PDMS or nanocomposite material.

Hydrophobic properties of the treated stones are also summarized in Table 1. Results indicate that all the stone surfaces show hydrophobic behavior (contact angle measurements $\alpha > 90^\circ$) after the treatments. It's worth to highlight that nanocomposites-coated stones showed higher hydrophobic properties than polymer-coated stones. It may be due to the homogeneous distribution of NPs in the polymer matrix which increase the hydrophobic nature of PDMS.

Table 1. Overall chromatic variations and contact angle measurements of treated stones.

Samples	ΔE^*	α (°)
PDMS_LS	4.4 (± 0.2)	111 (± 1)
Zn-Zr-PDMS_LS	3.9 (± 0.1)	131 (± 2)
PDMS_B	4.4 (± 0.5)	128 (± 1)
Zn-Zr-PDMS_B	4.8 (± 0.2)	136 (± 2)
PDMS_M	4.9 (± 0.1)	98 (± 2)
Zn-Zr-PDMS_M	4.8 (± 0.1)	107 (± 3)

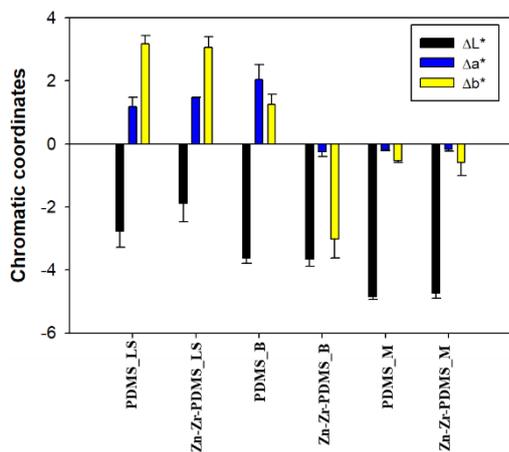


Figure 4. Chromatic coordinates of treated stones.

Moreover, preliminary data concerning capillary absorption tests confirmed that treated stones exhibited water repellent behavior. As can be seen in the Table 2, CA values (related to the first 30 minutes) are affected by both treatments (polymer as well as nanocomposite), while it was possible to note some reduction of Qf value compared the untreated stone at the end of the test (about 96 h). So, it seems that the treatments, especially with nanocomposite coating have long-term water resistant activity. The results are in good agreement with hydrophobic properties of treated stones. In addition, vapour permeability was preserved at acceptable levels upon treatment with ZrO_2 -ZnO-PDMS nanocomposite. Hence, all these results suggest that the newly prepared coating can be considered as a promising protective material.

3.2 Analysing the self-cleaning properties

As reported in the introduction, evaluation of the self-cleaning effectiveness of the newly prepared coating is one of the main aspect of this research study.

Figure 5 shows (as an example) the behavior of Lecce stone before and after the test. The different behavior of stone treated with the nanocomposite and with plain PDMS can be observed even by naked eye.

In order to evaluate the self-cleaning effect of the coatings, discoloration test was performed on the treated stones. After the application of MB solution on the treated surface, the specimens were exposed to UV irradiation. A quantitative evaluation of the self-cleaning behavior of ZrO_2 -ZnO-PDMS on the different stone was obtained by calculating the discoloration parameter D^* , which was determined at two different time intervals (see Figure 6). It is related to the variation of b^* coordinate (CIELAB space)

Table 2. Maximum Water Absorbed per unit area (Qf, mg/cm²), Capillary Water Absorption Coefficient (CA, mg/cm² s^{-1/2}), and values of the Water Vapor Permeability of untreated and treated samples.

Samples	Qf in mg/cm ²	CA in mg/cm ² s ^{-1/2}	Permeability in g/m ² 24 h
LS	518,74 (±9,62)	8,73 (±0,57)	236 (±9)
PDMS_LS	479,04 (±8,16)	4,63 (±0,50)	185 (±6)
Zn-Zr-PDMS_LS	434,18 (±6,68)	2,22 (±0,54)	174 (±4)
B	431,57 (±12,34)	2,12 (±0,21)	159 (±4)
PDMS_B	346,66 (±10,49)	1,53 (±0,44)	107 (±4)
Zn-Zr-PDMS_B	263,19 (±13,49)	1,03 (±0,01)	95 (±5)

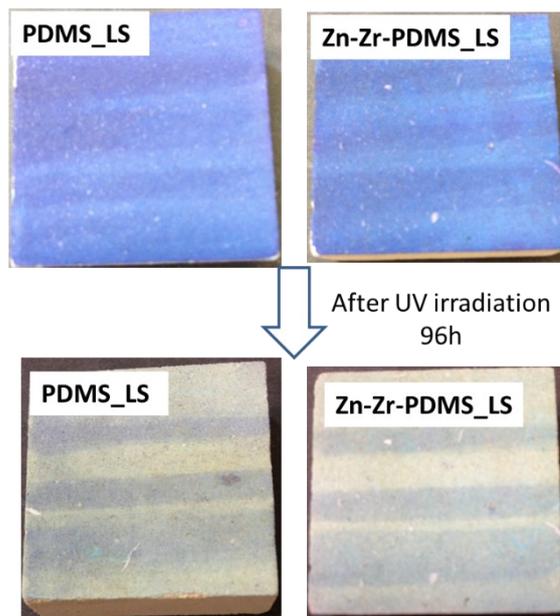


Figure 5. Images of LS before and after the self-cleaning test.

and corresponds to the amount of MB removed from the coated surfaces.

This test provided quite similar behavior for LS and B: the coating containing doped NPs showed a higher effectiveness than the plain PDMS coating. For instance, the discoloration factor related to the new coating is about double compared to PDMS (at the end of the test: $D^*_{PDMS} \sim 20\%$, $D^*_{nanoc} \sim 40\%$ both for LS and B) and as reported in the literature, NPs as well as doped NPs with PDMS coating have been used as a self-cleaning protective coating due to their photocatalytic performance under UV light (when the presence of NPs, the discoloration factor is always higher than PDMS) [1], [16], [25]. The new coating showed even better results when applied on Marble surface, as the discoloration factor was around 70 % after 96 hours of UV irradiation. The results tally with the reported literature [1]. Nevertheless, it should be noted that even plain PDMS display better performances on marble specimens if compared to the other considered stones. Although it is difficult to reliably compare the effectiveness of a treatment on different substrates, due to the different original stone properties (e. g. absorbability of the products, porosity, etc.) that may affect the

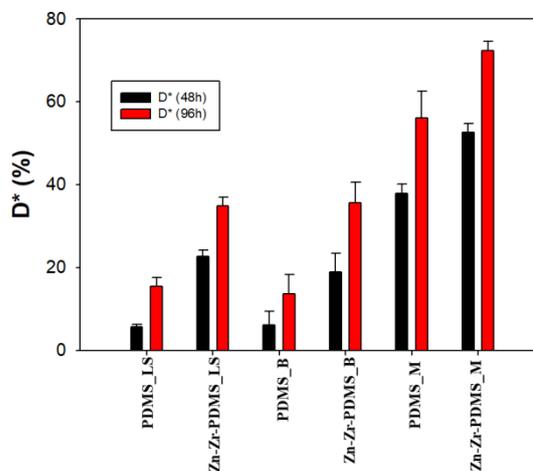


Figure 6. The discoloration percentage (D^* (%)) after UV exposure.

final performance, the experimental data discussed above indicate that the nanocomposite coating (ZrO₂-ZnO-PDMS) provides better results in terms of the self-cleaning effect when compared to plain PDMS.

4. CONCLUSIONS

In order to enhance the photocatalytic properties of ZnO, ZrO₂-doped ZnO NPs were synthesised in the laboratory. After that, the nanocomposite ZrO₂-ZnO-PDMS was synthesized, applied on different stone substrates (LS, B, and M), and its protecting behaviour was compared to the well-known PDMS.

The morphological analysis suggested that prepared doped NPs have spherical shape, very small sizes (15-30 nm). This small size of the particles is effectively involved in providing great performances of the prepared coating. For instance, the results of contact angles, chromatic variations, capillary absorption and water vapour permeability measurements indicate satisfactory protecting behaviour of the resulting coating.

Moreover, surface analyses suggested that nanoparticles included into the binder matrix are homogeneously distributed on all the stone surfaces. Furthermore, the new coating (ZrO₂-ZnO-PDMS) showed better results when compared to PDMS in terms of self-cleaning effect due to UV irradiation, which represents one of the most important result of this research work. Further experiments are still in progress to better assess the nanocomposite properties.

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