NEW NANOMATERIALS FOR THE CONSERVATION OF HISTORIC LIMESTONE BUILDINGS

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**Purpose:** Generate a tool for the preventive conservation of Cultural Heritage based on models of artificial intelligent.

[Link to more information](https://www.upo.es/investiga/art-risk)

**Art-Risk**

[@ProyectoArtRisk](https://www.upo.es/investiga/art-risk)
Stone damage

Weathering forms

Decay

Decay

Weathering forms

Degradation factors

Degradation

Lack of conservation

Conservation

Degradation factors

Vulnerability

Maintenance and/or Restoration
Façade of Santa Calatina Church (Seville)

Gothic-Mudejar church (1350-1399)
Monument (Gaceta 08/09/1912)

Main façade proceeded from Santa Lucía church (XIV century) and was placed in its current location in the XX century.
Main processes carried out in a restoration of historic and contemporary stone buildings:

- Lack of cohesion → CONSOLIDATION
- Biodeterioration → PROTECTION
Requirements for consolidation and biocide treatments

- Effectiveness
- Durability
- Penetration, without generating interfaces between the treated and untreated areas
- Maintain the porosity of the stone to allow its breathing and water circulation
- Chemical compatibility, avoiding chemical reactions or the formation of layers on the substrate
- Avoid altering the aesthetic aspect, both in its color and its brightness. Besides, the treatment must maintain its properties over time, without deteriorating due to the effect of external agents
New nanocomposites based on NPs Ca(OH)$_2$ doped with QDs ZnO

NPs Ca(OH)$_2$ (50-600 nm)
- Chemical compatibility with carbonated materials
- Durability
- Effectiveness
- Application with different solvents

QDs ZnO (8 nm)
- Fluorescence

PATENT P201831200
Characterization of Nanodots

Fluorescence of ZnO QDs

Cross section of a sample treated by the upper surface (white arrows)

Stone samples: properties

Limestone from Puerto de Santa María quarry (Cádiz)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pore diameter (μm)</th>
<th>Open porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcarenite</td>
<td>10-100</td>
<td>38</td>
</tr>
</tbody>
</table>
Nanodots were applied over the stone samples in ethanol suspension at concentration of 2.5 g/L.

Four doses of 0.15 mL/cm² were applied on stone surfaces.

The samples were dried during 20 days after last application at room temperature (24±2°C) to guarantee the end of the carbonatation process.
Not colour changes

Untreated

Treated with Nanodots

\[
\Delta E^* = (\Delta L^2 + \Delta a^*^2 + \Delta b^*^2)^{1/2}
\]
where \(\Delta L\), \(\Delta a^*\) and \(\Delta b^*\) characterize the variations between initial and final colour slabs defined by the CIELAB colour-system.

\(\Delta E^*<5\) for Cultural Heritage

\(\Delta E^*=2.04 \pm 1.3\)

The consolidation of treated limestones was studied by the peeling test. This assay was carried out using Scotch Cristal tape (3M) with 10 repetitions over the same location.

The percentage of consolidation (% Consolidation) relative to that of untreated samples was calculated according to Eq.:

\[
\% \text{Consolidation} = \frac{\text{TRM}_{\text{untreated}} - \text{TRM}_{\text{treated}}}{\text{TRM}_{\text{untreated}}} \times 100
\]

\% Consolidation = 92%
Discernibility and penetration depth

Treated with Nanodots

Untreated

Under UV light
λ=254 nm

Ag NPs
- Biocide

TiO\(_2\) NPs
- Photocatalytic property under UV light

Nanocomposite of Ag/TiO\(_2\)
Ag NPs improve the photocatalytic properties of TiO\(_2\) NPs, increasing their reactivity through the visible spectrum

Stabilizing agent
- Trisodium citrate
- Tetraethyl orthosilicate (TEOS)

Nanocomposites of
Ag@CIT/TiO\(_2\)
or
Ag@TEOS/TiO\(_2\)

PROTECTION AGAINST BIODETERIORATION
### Treatments

<table>
<thead>
<tr>
<th></th>
<th>HD</th>
<th>ζ (&gt;30)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>184±49</td>
<td>-17±2</td>
</tr>
<tr>
<td>Ag/TiO₂</td>
<td>94±33</td>
<td>-17±3</td>
</tr>
<tr>
<td>Ag@CIT</td>
<td>36±8</td>
<td>-63±3</td>
</tr>
<tr>
<td>Ag@CIT/TiO₂</td>
<td>52±11</td>
<td>-27±1</td>
</tr>
<tr>
<td>Ag@TEOS</td>
<td>5±1</td>
<td>-125±19</td>
</tr>
<tr>
<td>Ag@TEOS/TiO₂</td>
<td>120±16</td>
<td>-37±4</td>
</tr>
</tbody>
</table>

HD: Hydrodynamic diameter = NP size + solvation layer
ζ: Zeta potential = surface charge of NP in the dispersion

LIBS instrumentation set-up:

- Pulsed Nd:YAG laser 532 nm, energy: 27 mJ/pulse, pulse duration = 5 ns
- Focusing optics - planoconvex quartz lens, focal length 100 mm
- Collecting optics - quartz optical fibre
- Spectrograph – Echelle, spectral region of 200–850 nm
- Detector - ICCD camera, delay time (2.5 µs) and integration time (10 µs)
- All experiments performed in air under atmospheric pressure

PENETRATION DEPTH OF TREATMENT:
Last pulse-laser with Ag X Average depth of a crater generated by a pulse-laser

Sample treated with Ag@Cit NPs

Limestone from Utrera
1 pulse-laser = 10 µm

<table>
<thead>
<tr>
<th>Point</th>
<th>Nº pulse-laser</th>
<th>Penetration (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18</td>
<td>180</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>200</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>160</td>
</tr>
<tr>
<td>4</td>
<td>19</td>
<td>190</td>
</tr>
<tr>
<td>5</td>
<td>13</td>
<td>130</td>
</tr>
<tr>
<td>6</td>
<td>13</td>
<td>130</td>
</tr>
<tr>
<td>7</td>
<td>23</td>
<td>230</td>
</tr>
<tr>
<td>8</td>
<td>14</td>
<td>140</td>
</tr>
</tbody>
</table>

Average penetration depth: 170 µm
Sample treated with Ag@Cit/TiO$_2$ NPs

Ag(I) 338.289 nm

Ti (I) 521.0384 nm

Ag@Cit/TiO$_2$: penetration depth of 60 μm. Some isolated Ag NPs penetrate until 198 μm.

Colour changes ($\Delta E^*$): colorimetry

The treatments were applied at concentration of 0.3 mg/mL, except to Ag NPs: 0.03 mg/mL

### Effectiveness: Biofilm Extension

<table>
<thead>
<tr>
<th>Product</th>
<th>λ (nm)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>420</td>
<td>520</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>28.3±15.7</td>
<td>26.8±15.3</td>
<td>19.2±12.6</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.3±0.1$^+$</td>
<td>0.8±0.4$^+$</td>
<td>0.2±0.1$^+$</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>1.3±0.3$^+$</td>
<td>2.2±0.2$^+$</td>
<td>0.84±0.2$^+$</td>
<td></td>
</tr>
<tr>
<td>Ag@TEOS</td>
<td>3.6±0.8$^+$</td>
<td>0.8±0.7$^+$</td>
<td>0.5±0.3$^+$</td>
<td></td>
</tr>
<tr>
<td>Ag@TEOS/TiO$_2$</td>
<td>2.5±1.2$^+$</td>
<td>5.6±1.2$^+$</td>
<td>3.9±1.4$^+$</td>
<td></td>
</tr>
<tr>
<td>Ag@CIT/TiO$_2$</td>
<td>4.6±1.3$^+$</td>
<td>4.0±1.0$^+$</td>
<td>1.9±0.6$^+$</td>
<td></td>
</tr>
<tr>
<td>No treated</td>
<td>20.5±11.5</td>
<td>24.9±11.9</td>
<td>19.1±10.8</td>
<td></td>
</tr>
</tbody>
</table>

$^+$P-value<0.05

**BIOFILM THICKNESS: Optical coherence tomography (OCT)**

**PRE-WEATHERING TEST**

- OCT Image
- Doppler Image

**POST-WEATHERING TEST**

- OCT Image
- Doppler Image

- Untreated
- TiO2

**Maximum thickness of 0.03 mm**

Conclusions

• Preliminary studies on the causes of the decay in monuments of Seville (Spain) conclude that biodeterioration, together with other weathering elements, is major risk factor that leads to the deterioration of our Cultural Heritage constructions.

• Regarding consolidant treatments, we have developed a new nanocomposite based on calcium hydroxide and zinc oxide nanoparticles with fluorescence properties that allow us to check the surface intervened and measure easily the penetration depth of the treatment under ultraviolet light. Additionally, this product has good consolidation properties.

• In the case of biocide, silver and silver/titanium dioxide nanoparticles have shown a high capability to inhibit algal biofilms. The use of correct concentration allowed to avoid undesirable aesthetical changes while, in other cases, it is possible to use other nanoparticles with similar results, i.e., zinc oxide nanoparticles.

• LIBS has shown good results for measuring the penetration depth of metals nanoparticles and nanocomposites inside substrate stone.

• Optical coherence tomography (OCT) and multispectral images have been useful to analyze the thickness layer and extension caused by biofilms over the surface stone.
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Art-Risk

@ProyectoArtRisk
“thank you for your attention :)”

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