

Nanoparticle Technology Saves Cultural Relics: Potential for a Multimedia Digital Library

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***Abstract:** This short paper discusses how cultural and heritage works of art can be restored with the latest nanoparticle technology after degradation over time as well as damage by unnatural causes, such as flood and fire. Because of the importance of these works of art, this paper also discusses the potential of multimedia digital libraries for building, organizing, and distributing the information related to the conservation and restoration of these objects as well as the description and annotation of these works.*

INTRODUCTION

What does “conservation” mean?

The term “conservation” may have many different meanings in different fields. For example, art conservation versus book and manuscript conservation, versus managing the physical environment (ecology). Every intervention directed to the restoration and safeguard of works of art is commonly considered as a conservation treatment. For example, conservation can involve the cleaning procedures set up by chemists, or the photo documentation of the preservation of historical memory. For the appropriate conservation of works of art, even the lighting systems in a museum or the control of the visitor’s movements in a site should be monitored.

During the last decades, the scientists’ contribution to conservation work related to cultural heritage has grown rapidly. The knowledge in conserving a work of art is not limited to the historical and the semiotic analysis. Nowadays, conservation requires a deep knowledge of material science and nanotechnologies since it is not possible to prevent all natural aging of the works of art. Thus, chemists and physicists can contribute greatly to the “controlled death” of works of art because they can provide useful and reliable predictions of the degradation of these works of cultural heritage.

The scientists’ contribution

Chemical degradation, which induces the flaking of paintings and deterioration from rain, wind, dust, and other environmental causes, is mainly responsible for the weakening of the porous structure and the surface layers of the materials used in works of cultural heritage. In these situations, restoration is essential to the works of art. Most of interventions allow the reinforcement of the porous structure and the consolidation of the surface layer. Protective treatments, after cleaning and consolidation, confer longer life for the works of art. Restoration fights the opacitization of the surface by minimizing the light scattering effects, and surface protection strongly reduces the degradation from pollutants and water condensation. Having

mentioned these benefits, on the other hand, every restoration treatment must be considered as invasive and in certain cases disruptive.

Currently, most restorers are not correctly trained in restoring works of arts. They remove chemicals such as fat, salts, varnishes, and pollutants from the surfaces of the works of art by using mostly chemical and mechanical methods. These also affect the substrates of the works. Moreover, chemicals for consolidation and protection are used for improving the physico-chemical and mechanical features of the materials. In these cases, new materials are introduced within the porous structure of the works of art. Thus, this process modifies greatly the original physico-chemical characteristics of the objects, and makes it difficult to predict the lifetime of the restored materials.

In the following, we will introduce briefly our innovative restoration of works of art (frescoes, oil-paints, paper deacidification). A few simple principles for obtaining the best results in a restoration should be stressed:

- The treatment should be reversible so that one can go back to the original status of the work of art at any desired time;
- all the applied chemicals must ensure the maximum durability and the chemical inertness;
- the applied chemicals must invert the degradation processes without altering the chemical composition of the works of art and their physico-chemical and mechanical properties.

NANOPARTICLE TECHNOLOGY AND RESTORATION

An innovative point of view

In the last decade, great importance has been to the reversibility of conservation/restoration treatments. We know now that complete attached reversibility does not exist. Therefore, methods based on materials that are compatible with the work of art should be preferred, so that the original features of the materials are only slightly changed.

At the end of the 19th the practice of restoration methods that do not inhibit further future interventions was considered acceptable. During the 1960s several chemicals such as polymeric resins were synthesized and applied as a consolidation or protection agents. The accepted idea was that these substances could be removed at any time, leaving a completely unaltered substrate. Yet, numerous experiences gained in recent years have shown that this assumption was completely wrong and consistent damage is present in all restored art works. Most of the works of art restored by using polymeric resins suffered devastating action promoted by these polymers. Unfortunately, the removal of these polymers is not easy and in some cases is not even possible.

The prediction of the physico-chemical stability of most organic chemicals not compatible with the substrate is really difficult. Chemicals usually considered reliable are in most cases harmful in a long term. Thus, we are in favor of the “compatible as possible” approach in restoration and conservation of cultural heritage artifacts. This means the use of chemical analogues products or very similar to the original ones. This strongly reduces any risks connected to the low compatibility among different materials. Only inorganic materials should be used for conservation treatments of stones, wall paintings, and so on. In this “similia

similibus curantur” approach, the concept of *reversibility* and *compatibility* assumes the similar meaning.

The CSGI’s contribution

The Center for Colloid and Interface Science (CSGI – Consorzio interuniversitario Sistemi Grande Interfase) of the University of Florence is a non-profit organization funded by the Ministry of Instruction of University and Scientific Research (MIUR) of the Italian Government. It is currently involved in several physical chemistry projects related to the conservation of cultural heritage.

Aside from the enormously rich cultural resources in the city of Florence, it is one of the most suitable places with most appropriate "environments" for our conservation studies. For example, after the 1966 Florence flood, the research group founded by Prof. Enzo Ferroni and currently directed by Piero Baglioni was the first Academic Institution that applied a rigorous scientific approach to the investigation of cultural heritage degradation. Together they have formulated rigorous conservation procedures based on solid scientific ground.

The CSGI group has developed the most advanced nanotechnology-based methods for the restoration of wall paintings. These include methods for cleaning and removal of resins from wall and oil paintings, for frescoes consolidation, and for paper de-acidification. Currently these methods are used in many parts of the world. Active global collaborative activities are growing fast and they include some of the most significant art, cultural and museum institutions in the world as including:

- Demark - National Museum of Denmark
- France - Louvre Museum – France
- Italy – Many art, museum, and cultural institutions, including
 - Uffizi Museum, Florence
 - European Center for the conservation of the Cultural Heritage, Venice.
 - Opificio delle Pietre Dure di Firenze, Laboratorio Scientifico, Florence.
- Mexico
 - Amparo Foundation, Puebla, Mexico.
 - INHA- National Institute for Conservation of the Mexico Cultural Heritage.
- Switzerland - Department of Applied Art, University School of Italian Switzerland (Supsi), Lugano.
- USA - The Getty Conservation Institute, Los Angeles.

Numerous restoration activities have been carried out with our scientific advice and using the innovative methodologies developed at the CSGI Laboratories. The specific artifacts include: *Masaccio's* wall paintings in *Cappella Brancacci*, and *Beato Angelico's* wall paintings in *San Marco Abbey*, in Florence, *Piero della Francesca's* wall painting in *Arezzo*, etc.). Figure 1 shows both the pre- and post-restoration of these three paintings.

CSGI expertise is also related to the characterization



Figure 1. The difference between pre- and post-restoration using the nanoparticle technology method on three Italian wall paintings

of pigments, dyes, and binders used for wall or easel paintings, and also of the degradation products, such as salts, varnishes and aged adhesives present in stones, wall paintings, paper and wood.

A short review of the results obtained in the last ten years is provided in the following section. Readers are referred to more references provided at the end of this paper.

Nanotechnology for wall painting restoration

Calcium hydroxide is probably the best remedial treatment for reinforcing wall paintings since it is physico-chemical compatible and, moreover, it is the original binder used by artists. Unfortunately the poor solubility of calcium hydroxide in water has prevented the use of lime water. More concentrated systems, using lime as binder, could be prepared as a dispersion in water. Yet, lime dispersions in water are not stable. As a result, white glazing over painted surfaces forms.

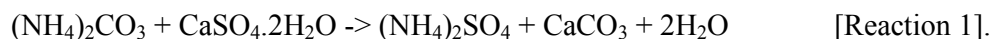
Ca(OH)₂ nanoparticles have been recently synthesized, and stable dispersions in nonaqueous media were obtained by selecting proper solvents. Scanning and Transmission Electron Microscopy (SEM and TEM) showed crystalline, hexagonally shaped, nanoparticles with hexagon sides in the range 100-300 nm. Atomic Force Microscopy (AFM) evidenced that the thickness were in the range 2-40 nm. Calcium hydroxide stable dispersions were successfully applied, instead of organic glues, as fixatives to re-adhere lifted paint layers during the restoration of the wall paintings by *Santi di Tito* in the Cathedral of Florence, *Filippo Lippi* in the Cathedral of *Prato*, stone materials in the *Santa Prisca in Aventino* Apse Church in Rome, wall paintings by Conrad Albrizio in the State Exhibit Building Museum of Louisiana, etc.

The Ferroni-Dini method

The formulation of calcium hydroxide nanoparticle derives from the Ferroni-Dini method. Wall paintings sulphatization is mainly due to the slow transformation of the binder CaCO₃ into selenite (CaSO₄.2H₂O) by the combined action of atmospheric SO₂ and O₂. Until thirty years ago, the most common method to rescue sulfated frescoes was the detachment of the fresco itself. This detachment allowed the rescue of the painting, but most of the painted surface was lost forever (in some cases up to the 30-50%) during the detachment. In order to overcome these problems, Enzo Ferroni and Dino Dini elaborated a new method to clean and consolidate wall paintings affected by sulphatization. The method consists in two steps:

1. The application of a saturated solution of ammonium carbonate, (NH₄)₂CO₃, and
2. the treatment with a barium hydroxide solution, Ba(OH)₂.

The first conservation treatment involves this chemical process:



The selenite that forms the patina or the small blisters shown in the photos of this report is converted into calcium carbonate with the formation of water soluble (NH₄)₂SO₄. The paint is washed with water to remove the soluble ammonium sulphate and a reconsolidation of the wall painting is performed in the second step of the Ferroni-Dini method. Reconsolidation is necessary as calcium carbonate, formed during Reaction 1, is powdery, when not in a binder form. Moreover, the reversion of selenite to calcium carbonate produces a volume

contraction leading to the formation of empty spaces, that result in an increment of the porosity of the first wall layers, and then in a decreasing of its cohesion and compactness. The second step of the Ferroni-Dini method is the application of the barium hydroxide, Ba(OH)₂, solution by means of wood poultice compresses. This compound plays a double effect: it eliminates the ammonium sulphate in excess and produces a strong consolidation of the wall painting. The chemical reaction between ammonium sulphate and barium hydroxide is:



The ammonium sulphate is converted into the inert and very insoluble BaSO₄, while the volatile ammonia and water evaporate from the wall. BaSO₄ crystals partially fill the empty spaces created by the reconversion of selenite into calcite. Indeed, the consolidation of the mural painting is made by another series of chemical reactions originated by the barium hydroxide.

The consolidation effect originated by the barium hydroxide technique is due to two different chemical reactions. The excess of Ba(OH)₂ adsorbed within the wall is subjected to carbonation according to the reaction:



The barium carbonate crystals act as 'filler' for the empty spots created by the reconversion of selenite into calcite, and, again, produce cohesion. There is another source of consolidation due to the following reaction:



The presence of calcium hydroxide indicates that the treatment with barium hydroxide converts the non-binder calcium carbonate into new and 'fresh' calcium hydroxide (slaked lime). The original binder is formed *in situ* and begins a slow setting process - called *carbonation* - that slowly increases the cohesion of the paintings week by week, month by month.

Nanoparticles treatment is the logical evolution of the Ferroni-Dini method, and can replace it in most cases with some advantages. The Reference section contains several CSGI conservation patents.

RESTORATION AND POTENTIAL FOR A MULTIMEDIA DIGITAL LIBRARY

Since 1984, Ching-chih Chen has been actively involved in using cutting-edge multimedia technologies to create multimedia electronic contents of significant cultural and historical topics and finding innovative ways of organizing, presenting and disseminating these contents. Her efforts include the award-winning interactive videodisc as well as multimedia CD-ROM products, entitled *The First Emperor of China*, both published by the Voyager Company. Since 2000, her *Chinese Memory Net (CMNet)* project [Chen, 2001a], supported by the US National Science Foundation's International Digital Library Program (NSF/IDL/P/IIS-9905833), is her beginning effort in creating a model for a Global Digital Library (GDL) in cultural and heritage areas. This global consortium effort has gathered momentum recently with various possibilities of global collaborative activities [Chen, 2001].

Given the subject matter of the image contents as well as the importance of the restored images, the University of Florence's CSGI group is one of the natural and productive collaborative partners with GDL for several reasons. The following highlights only a few obvious ones:

- The restoration activities, as stated earlier, involve some of the world's best known art and museum institutions, and the art works under restoration are of great significance to scholars, researchers, and art-lovers of the world. Thus, not only is the restoration essential, but also the information related to the art works is of great importance. The descriptive information and annotation for each art work need to be properly prepared and organized in order to be retrievable and useful to scholars and students of art history.

- In following the kind of restoration process used by the CSGI group, it is obvious that its restoration projects will yield significant amount of information related not only to how the specific art works were damaged and then restored, but also on the proper conservation methods used for these cultural heritage materials. To document these processes digitally would be the most advanced and effective way to safeguard this kind of vital information and transmit it to the future generations for scholarly and educational purposes.

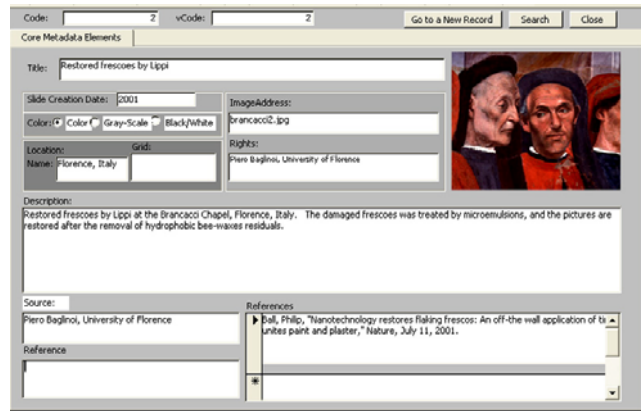


Figure 2. A baseline database record of a restored image

Our collaborative multimedia digital library activity, Project Restore, can be an integral part of the *Global Memory Net* project, and thus benefit from much of the R&D results of the *CMNet* project, including image and video retrieval, metadata, etc. Figure 2 shows the baseline database record of an image. This is in the similar database format of the Emperor images of the *CMNet*, and can be converted to comply with OAI-PMH standard easily. The complete collection can be a part of the Global

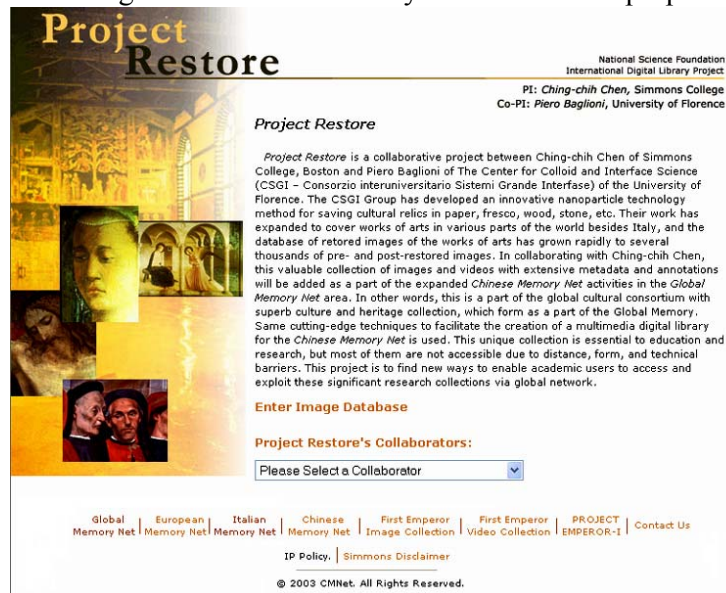


Figure 3. Preliminary Home Page of Project Restore as it links to other memory sites

- Furthermore, existing tools and techniques in image retrieval can further benefit Project Restore. Figure 4 shows that the valuable metadata information on the restoration images can be used for various effective image retrievals. For example, images can be retrieved by the more conventional searches by title, keyword, subject, location, etc., as well as by the semantic sensitive content-based image retrieval techniques [Chen, 2002; Wang, 2002; Wang, 2003] by color, shape, semantic descriptions, etc. Thus, related images before and after restoration can also be retrieved promptly and effectively.

CONCLUSION

In the digital domain, progress has been made in areas of digital restoration of cultural and heritage materials (Seales, 2003). However, the importance of conservation and restoration of works of art is unquestionably recognized by all scholars and citizens who appreciate the world's cultural and heritage contents. While we have introduced an innovative nanoparticle technology of the

[Chen, 2002; Wang, 2002; Wang, 2003] by color, shape, semantic descriptions, etc. Thus, related images before and after restoration can also be retrieved promptly and effectively.



Figure 4. Screen showing traditional and content-based retrieval of images

CSGI Group of University of Florence to save culture relics, we have also elaborated on the potential of having the rich multimedia information on both the restoration process and the restored and conserved works of arts for developing a valuable digital library as what the collaborative Project Restore is beginning to undertake. Such photo documentation is also an invaluable teaching tool for conservation students as well as practicing conservators. This interdisciplinary collaborative activity is in line with the recommendations of the *DELOS-NSF Working Group on Digital Imagery for Significant Cultural and Historical Materials* [Chen, 2002a].

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