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Nanotechnologies for Cultural Heritage: Nanodiamond for Conservation of Papers and Parchments

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Abstract. In this paper we report some tests regarding the feasibility of nanodiamond to act as a cleaning/consolidation agent of papers and parchments. We carried out a series of treatments aiming to develop innovative approaches for de-acidification, cleaning and consolidation. Dispersions of nanodiamond have been used as de-acidification agents of ancient papers showing the ability to sensibly reduce the acidity of the paper without using any alkaline base. Similar dispersions have been used for cleaning processes and nanodiamond demonstrated an outstanding capability to clean ancient papers and parchments avoiding the use of any solvent and surfactant. Moreover interesting results were obtained by using nanodiamond as consolidation agent. In particular, artificial aging by UV exposition was appreciably contrasted when samples were preliminarily submitted to a treatment by nanodiamond. This outcome was demonstrated in papers and parchments by Raman spectroscopy analyses that evidenced the property of nanodiamond to be an excellent UV-scavenger.

INTRODUCTION

The development of advanced materials and methodologies for effective restoration of artworks is an evolving challenge in the field of cultural heritage. Restoration as a whole is a complex process, consisting of different procedures depending on the type of the masterpiece, the fragility and the complexity and inherent uniqueness of the work. The materials and techniques used for its creation and current state of conservation also determine the protocol to be followed for an effective restoration of the piece.

Art restoration typically foresees a large use of chemicals, especially in the cleaning and consolidation steps[1,2], and in the last fifty years big amounts of surfactants and of polymers have been effectively adopted for treatments related to such steps. However, the excessive use of surfactants such as sodium dodecyl sulfate (SDS), may result in some cases a too aggressive treatment, which removes not only pollution and degradation products but also pigments or water, thus causing alteration of the chemical matrix of the artwork. On the other hand, the massive use of vinylic, acrylic, and silicone-based polymers and of their copolymers, which for a long time has been considered "reversible"[3] (that is, the solvent used for their application could be later used for the removal of the applied resins), was found inducing severe modifications on the artifact. Such alterations range from the changing of

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the natural hydrophilicity, to the water vapor permeability and the surface wettability of the artwork, all anyway provoking an acceleration of the aging process[4,5]. Moreover, due to chain scission and cross-linking reactions polymers themselves are subjected to degradation, which makes the solubility of the polymers dramatically decreased, and their removal difficult or, often, not possible[6,7,8].

In order to solve these problems, researchers are putting efforts to reduce or cut out chemicals, by introducing new strategies and solution for artworks restoration. Recently, significant advances have been made by the use of nanomaterials and of the ground-breaking innovations generated by nanotechnologies. In such a context, the class of nanodiamonds represents nowadays one of the more exciting material to be used in the field of cultural heritage.

Nanodiamond (ND) particles produced by dynamical synthesis have sizes in the range 5-10 nm and are characterized by a series of attractive properties. The holding of physicochemical properties superior to those of bulk diamond and the presence of additional features make this new entry of the nanocarbon family an increasingly important protagonist of nanotechnology research[9-14]. In this work we used ND as consolidating and cleaning agent for restoration of ancient papers and parchments. In particular, three types of treatments are here reported: deacidification of papers, cleaning of papers and parchments, and consolidation of papers and parchments.

EXPERIMENTAL

1. Materials and Methods

Detonation ND (DND) powders with primary sizes in the range of 5-10 nm were obtained from International Technology Center (ITC, USA). Before the use, DND powders were further purified and de-agglomerated[15]. Papers and parchments have been taken from a book from late XIX century (courtesy of S. Orlanducci). All the chemicals used are by Sigma Aldrich.

The artificial aging processes have been performed by inserting the samples in a UV-furnace for 24 hours. The structural features of the samples before and after the UV exposures, have been analyzed by Raman Spectroscopy, using a XploRA ONE™ Raman Microscope (Horiba JobinYvon) using a 785 nm excitation laser light and a 1200 gr/mm grating spectrometer coupled with an air-cooled scientific CCD.

TREATMENTS AND RESULTS

In the follow, a detailed description of the three types of DND-based treatments along with a discussion of the obtained results is reported.

1. Deacidification

1.1 Paper

In a typical experiment, a sample of ancient paper (1 cm x 1 cm) was immersed into 5 ml of 5% DND water dispersion and left stirring for 5 minutes at room temperature. The pH of the dispersion was measured before and after the treatment. Blank samples were prepared using the same procedure but using distilled water instead of the DND dispersion. The pH measurement was repeated 5 times for each sample.

For the pristine DND dispersions, a pH of 5.5 was measured. After the paper immersion in the DND dispersion, the pH decreased to 2.7 ($\Delta pH_W = 2.8 \pm 0.1$) whereas when the paper sample was immersed in distilled water (initial pH = 6.3), the pH of the solution decreased to 5.6 unit ($\Delta pH_W = 1.7 \pm 0.1$).

The pH measurements indicate the good performance of DND as deacidificant agent compared with the conventional washing processes used for papers.

2. Cleaning

2.1 Paper

The cleaning agent was prepared by dispersing 10 mg of DND into 100 ml of distilled water under sonication. Then, six pieces of ancient paper (0.3 cm x 0.3 cm) were gently dipped into the DND dispersion and treated with ultrasounds for 15 minutes.

Paper is mainly composed of cellulose fibres, that are linear polymers of glucose monomers linked by β-1,4-glycosidic bonds. The yellowing of ancient papers is mainly a consequence of the oxidation of such polymer chains. The oxidized products, acting as chromophores, selectively absorb light and produce the yellow coloration typical of ancient papers.

Our experiments pointed out as 1% DND water dispersion is particularly efficient in the removal of oxidized celluloses. In Figure 1 an ancient paper sample treated with DND is reported on the left, while the same treated with the only distilled water is shown on the right. As one can see, DND has the propriety to restore paper to its original colour without any use of surfactants or harsh chemicals.

Figure 1: Optical image of an ancient paper treated with DND dispersion (on the left) and distilled water (on the right).

2.2 Parchment

100 mg of DND were dispersed into 10 g of polyester matrix for producing a cleaning agent for ancient parchments. A 1 ml of ethanol was added to 100 mg of such nanocomposite, obtaining a soft viscous material to be used for the cleaning procedure. A small part of the produced resin was taken with a cotton swab and gently rubbed to the parchment surface. Immediately, the dirt over the ancient parchment has been adsorbed by the resin. In case of fungi the parchment has been rubbed for more time to ensure a quantitative mildew removal. After the cleaning, a cotton swab dipped in water was rubbed on the surface to remove any trace of resin.

Parchment is a material derived from animal skin and is mostly made by collagen, a natural biopolymer with molecular mass of 350 kDa. The aging of parchment is mainly due to protein degradation, like disulfide bond oxidation, hydrolysis of peptide bonding and skeletal deformation. Moreover, if not well preserved, parchments can undergo to fungal attacks.

The old parchment used in the present work is the hard cover of a book of the XIX century in a bad state of conservation. It showed several areas of diffused yellowing, and some spots with mildew growth. The cleaning process from fungi is a rather difficult step since they are generally strongly bounded to the collagen fibers and are hard to remove. Moreover, the cleaning method should not be too aggressive, in order to avoid the removal by mechanical abrasion, or the production of modifications into collagen fibers. By using the DND-based cleaning agent, we were able to remove most of the mildew present on the parchment without any apparent pigmentation loss, as it is possible to see in Figure 2.

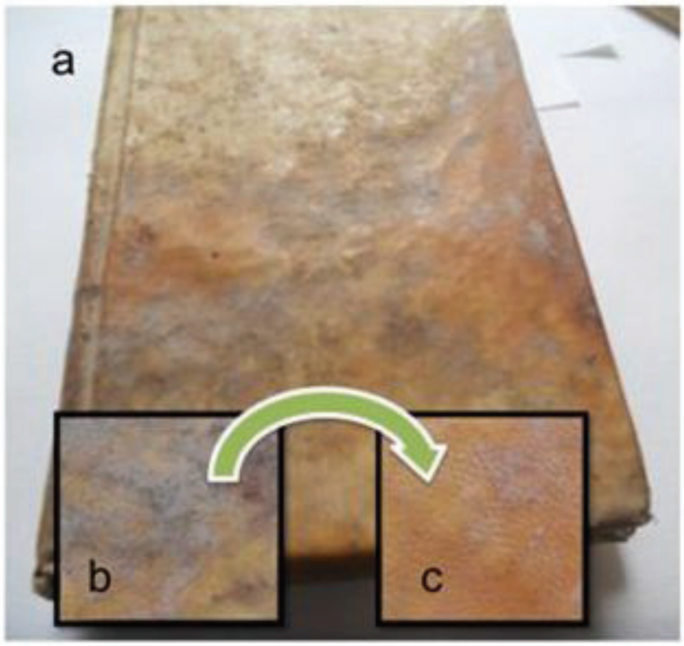

Figure 2: (a) General view of the parchment hard cover of the book; (b) optical image of the parchment before the cleaning; and (c) optical image taken from the same area after the cleaning.

3. Consolidation

For consolidation purposes, we used 1 % and 5% DND dispersions in water. Five samples of paper and five of parchment were treated by the 5% dispersion. All the samples were dried and submitted to UV radiation for 24 hours. Then they were analyzed by micro-Raman Spectroscopy by examining three different points for every sample. Spectra of not irradiated samples have been collected under the same condition and used as blank for comparison.

3.1 Paper

In a paper, cellulose is generally in a stable crystalline form for about 80%. The crystalline content of cellulose is a crucial parameter to establish the integrity and state of conservation of a paper. In fact, crystalline cellulose is quite stable, while the amorphous one is sensitive to hydrolysis and oxidation processes, which could lead to a shortening of polymer chains.

The exposure of cellulose to UV-light, acidic/basic conditions or to oxidizing environments leads to a dramatically decrease of the percentage of crystalline conformation of the polymer chains. In order to study the structural modifications of paper produced by UV radiations and the ability of DND to protect paper from light-induced damages, we performed Raman analyses of pristine paper and of UV-irradiated both pristine and DND-consolidated paper.

In Figure 3 the Raman spectra of three paper samples are reported: (a) pristine paper, (b) paper consolidated with DND after UV-irradiation, and (c) pristine paper irradiated with UV.

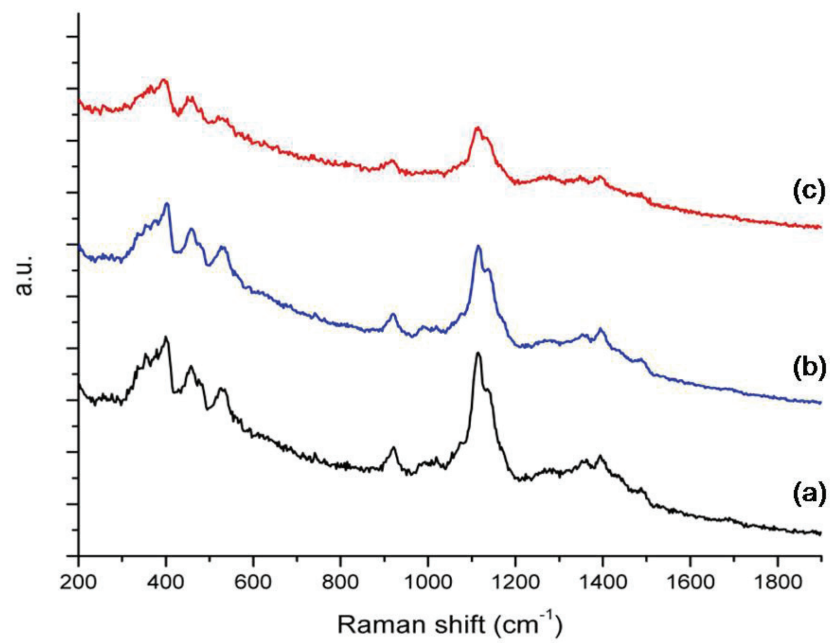

Figure 3: Raman spectra of: (a) pristine paper;(b) paper consolidated with DND after UV-irradiation; (c) pristine paper irradiated with UV.

For the pristine paper (spectrum a),a complex band corresponding to the bending of the (C-H) groups is notable between 1200 and 1500 cm^{-1}.These peaks are indeed strong indicators of the presence of hydrogen bonds, which are involved in the crystalline structure of cellulose. In particular, the bending of (CH_2COH) groups is seen at 1431 cm^{-1}, while at 1395 and 1360 cm^{-1}the signals corresponding to the bending of CH_2 groups are present. At about 1100 cm^{-1}there are the two unresolved peaks, one centred at about 1133 cm^{-1} ascribable to the stretching of hemicellulose (C-O-C) groups, while at 1113 cm^{-1}it is possible to note the band related to the vibration of (C-O-C) groups in both cellulose and hemicelluloses. Both these two signals are known to be of fundamental importance in the diagnosis of the preservation state of paper. Finally, at 1076 cm^{-1} the stretching of (C-O) groups of secondary and primary alcohol is visible while at 921 cm^{-1} it appears another diagnostic peak related to the crystallinity grade of paper.[16]

When paper is irradiated with UV light, several damages can be recognized from the analysis of the Raman spectrum (spectrum c). The peaks between 1200 and 1500 cm^{-1}, corresponding to the bending of the (C-H) groups, are broader and less intense. This effect is probably due to a loss of crystallinity of the fibres. Furthermore, it can be seen how the ratio between the intensity of the peak at 1113 cm^{-1}, corresponding to the (C-O-C) groups of cellulose and hemicellulose, and the intensity of the signal at 1133 cm^{-1}, corresponding to (C-O-C) groups in the only hemicellulose, is significantly decreased. Such occurrence can be explained as a dramatically enhancement of cellulose amorphization and hydrolysis promoted by UV-irradiation. This fact is also confirmed by the broadening of the peak at 921 cm^{-1}, related to a crystallinity loss of the fibers structures. Summarizing, we can say that 24 hours of exposure to UV light produces severe damages to paper since the Raman analysis clearly evidences that the cellulose fibres have partially lost their crystalline structure and that a noticeable amount of cellulose has been converted to hemicellulose.

The Raman analysis carried out on the spectrum taken from the UV-irradiated paper consolidated by DND (spectrum b) reveals as DND is effectively able to protect paper from the structural and chemical damages induced by UV irradiation. The peaks between 1200 and 1400 $cm^{-1}$are well defined, without loss of intensity or broadening effect, indicating that cellulose retained its native hydrogen bonds. The peak at 1113 cm^{-1} appears still sharp, with an intensity that is higher than the one of the peak at 1133 cm^{-1}. This confirms that hydrolysis of cellulose has been prevented by the DND action. Finally, it is noted that also the peak at 921 $cm^{-1}$is sharp and well defined, indicating that the most of cellulose is still in a crystalline state.

In conclusion, the obtained results highlight that DND is able to protect the cellulose from amorphization and chemical modifications induced by UV-irradiation, thus contributing to preserve the state of conservation of paper.

3.2 Parchment

The main component of a parchment is the collagen, a biopolymer composed mainly by amino acids with a triple helix conformation. Degradation of ancient parchments is the result of two different kinds of damages, namely structural and chemical damages. Structural damages involve the crystallinity loss of the parchment proteins. In particular, what happens is a structural deformation of the α helix and of the β sheet to a random coil state, and a skeletal deformation of the C-C in the *cis* and *trans* state, leading to a random conformation. Chemical damages involve instead the oxidation of the aminoacids, the hydrolysis of the peptide bonds and the attack from the sulfuric/nitric acid produced by pollution.

Even in the case of ancient parchments, the Raman spectroscopy is able to give fundamental information on their conservation state since it offers the possibility to monitor all the aging events, going to characterize at the molecular level the several damages suffered by parchment.

Figure 4 shows Raman spectra of three parchment samples. The spectrum (a) was taken from a pristine untreated parchment, the spectrum (b) refers to the same parchment after UV irradiation, while the spectrum (c) was acquired from the DND-treated parchment after UV irradiation.

In the spectrum of the pristine untreated parchment (spectrum a), it is possible to note several characteristic signals referring to the molecular structure of its fundamental constituent. In particular, at 1685 cm^{-1} the strong band corresponding to the helix amide stretching is clearly visible while at 1466 cm^{-1} the scissoring mode of the CH_2 group is found. The signals at 1342 cm^{-1} and 1292 cm^{-1}can be instead ascribable to the twisting vibration of CH_2 and $C(CH_2)$. The evident band at1265 cm^{-1} is attributable to the stretching of CN and of the amide and at 1172 cm^{-1} the C-C vibration of the skeleton of the polymer can be located. From 1025 to 1146 cm^{-1} we can see some complex bands corresponding to C-C vibrations: in particular at 1025$cm^{-1}$the stretching of (C-C) skeletal of the *cis* conformation, at 1120 and 1064 cm^{-1} the *trans* skeletal conformation while at 1143$cm^{-1}$the bands of the general vibration of (C-C) and of the deformation of (OH) groups. From 834 to 960 cm^{-1} there are well defined peaks corresponding to the rocking adsorption of the (C-H) groups: in particular the signals located at 960 and at 886 cm^{-1}

can be respectively ascribed to CH_3 and CH_2, while the peak at 834cm^{-1} can be attributed to the bending vibration of aromatic (CCH) groups.[17,18]

The spectrum of parchment after 24 hours of UV-irradiation (spectrum b) shows the occurrence of both structural and chemical damages. Regarding the chemical damages, there are several proofs of the hydrolysis mechanism of the peptide bond. In fact the bands at 1685 and 1265 cm^{-1}are broader and less intense respect the ones showed by the pristine parchment (spectrum a) and this can be due to the cleavage of the amidic bond. Moreover the bands in the 1429-1517 cm^{-1} region are very intense, probably due to the presence of free carboxylate in the damaged protein structure of the UV-irradiated parchment. The general broadening of the peaks between 800 and 1200 cm^{-1}can be instead ascribed to structural damages. The peaks related to the skeletal C-C vibrations of *cis* and *trans* conformations are broader and less defined, while at 1084 cm^{-1} the peak corresponding of C-C random coil vibration appears. These occurrence can be due to a loss of crystallinity after irradiation. Finally, the bands between 800 and 1000 cm^{-1}, corresponding to the rocking of C-H bond, result less intense and defined confirming a structural deformation of the proteins. Overall the Raman analysis revealed that the UV-irradiation severely damaged the parchment inducing hydrolysis of peptide bonds and producing structural skeletal alteration.

When nanodiamond is used as a consolidating agent, UV damages can be prevented. The analysis of the Raman spectrum of the parchment treated with DND (spectrum c) in fact reveals that the material seems totally unaffected by the UV irradiation. All the reference signals are well defined and there is no evidence of significant shift or broadening of the peaks. The spectrum indicates no significant hydrolysis of the peptide bonds nor evidence of skeletal damages or of any increase of the random coil structure.

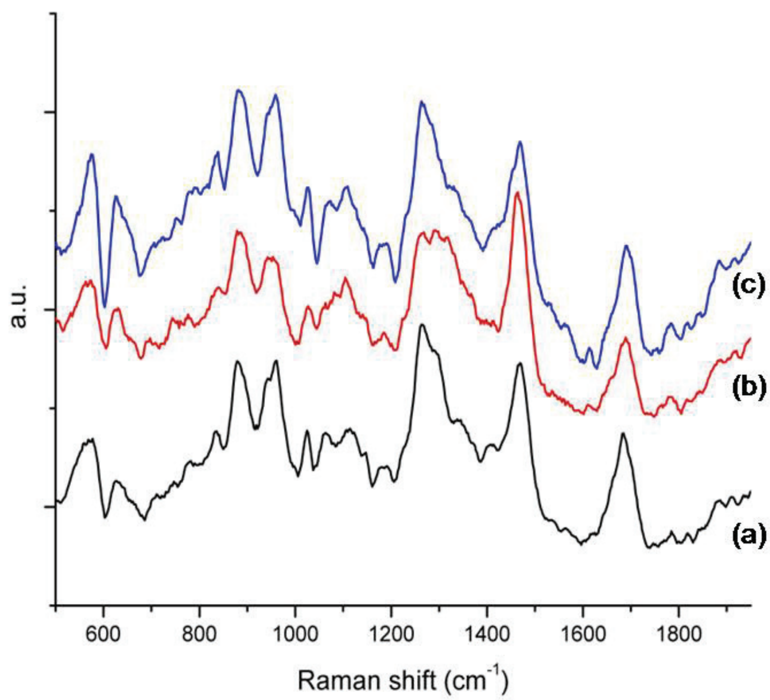

Figure 4: Raman spectra of: (a) pristine untreated parchment; (b) UV-irradiated parchment; (c) UV-irradiated DND-treated parchment.

CONCLUSIONS

The objective of this work was to test the feasibility of nanodiamond to act as cleaning/consolidation agent of papers and parchments. To this purpose, we carried out a series of treatments, developing innovative approaches for de-acidification, cleaning and consolidation.

The results prove the efficiency of nanodiamond to act as restoration agent of such naturally occurring materials, widely used across centuries as support for printed, painted, written and drawn images.

Dispersions of nanodiamond in water have been used as de-acidification agent of ancient paper showing the ability to sensibly reduce the acidity of paper without using any alkaline base.

Similar dispersions have been used for cleaning processes. DND demonstrated an outstanding capability to clean ancient papers, removing efficiently incorporated dust, debris, and the products of oxidation of cellulose. It is worth noting that these cleaning protocols have been developed avoiding the use of any organic solvents and surfactants that could dehydrate the paper.

For the cleaning of ancient parchment, nanocomposites formed by nanodiamond and polyester resin have been tested. The DND-based nanomaterials showed a remarkable capability to remove deposits of dust and traces of fungi and bacteria from the surface of ancient parchment.

Interesting results were obtained even about the possibility to use DND as a suitable consolidation agent. In fact, the artificial aging by UV exposition was appreciably contrasted when samples were preliminarily submitted to a treatment by DND. This outcome was demonstrated in papers and parchments by Raman spectroscopy that evidenced the property of DND to be an excellent UV-scavenger.

In particular, a sensible reduction of cellulose amorphization, oxidation or hydrolysis was detected for DND-treated papers while the degradation of the protein structure induced by UV light is sensibly reduced in DND-treated parchments. In this last case, DND was found to appreciably block hydrolysis and skeletal damages of the collagen constituting the parchment.

A further effect is that, in the presence of DND, the hydration of the fibers is completely restored. On the basis of all these outputs, the treatments by DND can be considered as an innovative, easy and efficient method of consolidation for papers and parchments.

The results of this research work that, at the best of our knowledge, represents the first application of DND to conservation of papers and parchments, open the way to a systematic use of nanodiamond and nanodiamond-based materials for conservation of artworks supported by such natural materials.

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