Degradation study of pigments through transient absorption and colorimetry

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***Abstract* – The application of non-destructive techniques in the field of cultural heritage is becoming fundamental to understanding degradation phenomena. In this study, Transient Absorption (TA) spectroscopy and colorimetry were exploited to explain the process which causes the degradation of some pigments, like Red Vermilion and cadmium yellow. The optical properties involved in the process are studied before and after exposing the pigments to UV light (365 nm). The study was carried out with particular attention to the ground state bleaching signals, directly connected to the formation of intra-gap trap levels responsible for the pigment degradation. First derivative reflectance spectra reveal the presence of these defects in the cadmium yellow, while the analysis of Tauc plots from Kubelka Munk function confirms the reduction of energy band gap due to UV exposure in the case of Red Vermilion. Transient Absorption turns out to be an important tool for the diagnosis of the conservation state of pigments.**

I. INTRODUCTION

Pigment degradation is a dynamic phenomenon that affects numerous materials in the field of Cultural Heritage. Several studies analyze this topic in detail, ranging from structural properties to vibrational fingerprints or colorimetric parameters [1–5]. The color change translates into the variation of optical characteristics, like absorption, transmittance, and reflectance which correlate the electronic properties or band structures with the macro effect on visible rendering.

Transient absorption (TA) spectroscopy is a proficient tool to understand pigment degradation because it can investigate the changes in the optical properties of a material [1,6]. In this technique, the probe transmittance through the sample is measured both in the presence and absence of the pump, as a function of relative time delay between the two pulses. Due to both linear and non-linear interactions, changes in the absorption spectrum of the materials are observed, providing information about the optical interaction, the electronic band structure, excitation and relaxation mechanisms, and defects.

Three main features can be distinguished in a TA experiment: Ground State Depletion (GSD) or Ground State Bleaching (GSB), Excited State Absorption (ESA), and Stimulated Emission (SE) [7]. In GSD the pump pulse excites the carriers from the ground state to the excited state, thus causing the decrease of the ground state population and the increase of the excited state population. This change in the relative population of the two states leads to a decrease, or bleaching, of the optical absorption, with a negative differential absorption spectrum. ESA occurs when the pump photons excite the carriers from the ground state to some excited intermediate state. Subsequent probe photons may excite the carriers from this intermediate level to a still higher energy level, thus producing additional new features in the absorption spectrum, with positive differential absorption signatures. Lastly, SE occurs when probe photons stimulate the radiative decay of carriers, previously excited by the probe, leading to the increase of the probe intensity transmitted through the sample, with negative differential absorption.

An in-depth analysis of ESA, GSD and SE signals is very useful to study the position of electronic bands, the presence of intermediate levels originating optical transitions and especially to highlight their variation associated with degradation phenomena.

In this work, we concentrate our attention on two case studies: the Red Vermilion and the yellow and orange cadmium showing the fundamental role of TA spectroscopy supported by the reflectance and colorimetry for the conservation and diagnostics of the artistic works.

A. Red Vermilion

The degradation of Red Vermilion (HgS) was widely debated in the literature. Recent works shed light on the possible phase transformation from alpha-HgS (red) to beta-HgS (black) during the darkening [1]. The process is accentuated in presence of halide impurities ions (chlorine) and the formation of metallic Hg was observed. At high concentrations, the appearance of chlorine-based compounds was not excluded as found in other works [8].

Starting from this assumption the aim is oriented to analyze the transient absorption properties in pure and 5M Cl-doped HgS samples, both under UV and without exposure conditions.

B. Cadmium yellow and orange pigments

The Cd-pigments are famous for being widely used by the Impressionists. The cadmium sulfide (CdS) has a golden yellow hue and it is present naturally in the mineral form of greenockite. During the 20th century, its synthesis began to be varied by inserting zinc to lighten the color, and selenium (cadmium sulfoselenide[9]) to increase the red hue, allowing the attainment of a range of colors from pale yellow to red, known by the generic term of cadmium pigments.
Although Cd-pigments are synthetic and have good covering properties, they undergo a rapid degradation process over time, which is largely described in the literature with alteration phenomena of the painted surface like chalking, lightening, flaking, spalling [10,11].
Mainly the degradation process is described with the formation of whitish compound as reported in [12–14], where the degraded white crust of the paints reveals the presence of carbonate, sulfate, and oxalate of cadmium.
To understand the degradation process of CdS pigment and the role of inner defects, we simulated artificial aging on two kinds of CdS commercial samples the yellow and the orange one through UV light exposure, showing the differences between the before and after treatment in terms of color variation and change in electronic properties. We used the pigments number 21040 (white-yellow) and 21080 (orange), bought from Kremer pigments and called them C-A and S-A respectively.

II. EXPERIMENTAL SECTION

A.Reflectance measurements

Reflectance measurements were performed by means of UV–Vis-NIR Agilent Technologies Cary 5000 spectrophotometer equipped with integrating sphere module. The reflection configuration at 10° measures the diffuse reflection of the sample with respect to a reference sample which is considered to have a 100% reflectivity. A calibrated source Illuminant D65 was used to determine the reflectance spectra and for calculating the colorimetric parameters.

B.Pump and probe measurements

Transient absorption measurements were performed with a pump-probe differential spectrometer (Ultrafast Systems HELIOS-EOS), with both pump and probe wavelengths generated by a Ti:Sapphire regenerative amplifier (Coherent Libra-F-1K-HE-230), which delivers 100 fs long pulses at 800 nm with 1 KHz repetition rate. The main emission from the regenerative amplifier was splitted into two branches: one sent to an optical parametric amplifier (Light Conversion TOPAS C), in order to generate the pump wavelengths (400nm), and the other sent to the sapphire plate of the HELIOS spectrometer, where multicolor probe beam was generated by means of white light supercontinuum generation.

C. Articial ageing process

The Red Vermilion samples were treated under the UV light of a LED at 365 nm (emission with Lorentzian profile having full width half maximum of 10 nm), under constant power density of 10 mW/cm^2, for time ranges between 0 and 200h. To deepen the study on the darkening process of Red Vermilion we realized synthetic samples doped with Cl^- (5M of NaCl solution) with the purpose to study transient absorption properties and simulate the effect of this catalyst agent. We report the assigned nomenclature of samples linked to the molar concentration: 0.00M NaCl called "pure" and 5M NaCl called "5M", and after the UV exposure we added the term "UV" in the previous nomenclature. We exposed the HgS pure sample for 148 h and HgS 5M for 20 h.

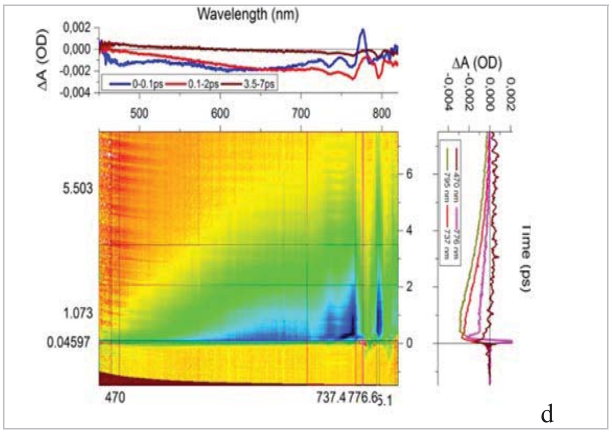
The Cd-pigments were exposed to UV exposure realized by Hg lamp, with wavelength at 365 nm, for 56 hours with a density power of 7mW/ cm^2. The artificially aged samples were called with the initial C or S to indicate the yellow or orange one, followed by the "UV" term to express the UV exposure and the total time of exposure (56h).

III. RESULTS AND DISCUSSIONS

A. Red Vermilion

Fig. 1. reports the spectrograms of raw and UV-irradiated pure HgS samples. The false color scale of the spectrograms shows a differential absorption signal measured in optical density (OD) ranging from positive (red color) to negative (blue color) values.
Pure HgS sample presents a short positive signal at 784 and 806 nm and a short negative signal at 670 nm closed after 6 ps and a combined signal at around 480 nm with an initial short negative contribution of around 1 ps which converts to a positive signal of about 10 ps. The application of UV light to the samples changes the characteristic decay time of the revealed signals that moved in the ns range drastically. In particular, a long ESA is revealed at 480 nm and long bleaching at around 800 nm. The latter assumes a very similar trend as compared to metallic Hg, one of the photo-degradation products found in literature, which presents a "long-lived" negative signal for all the explored wavelengths. The reported results suggest the formation of a HgS phase upon UV irradiation with spectral features similar to metallic Hg. Concerning the presence of chlorine ions

(fig. 1 c and d), they seem to not change the structure of the alpha-phase, since only small variations in the GSD spectra and characteristic decay times are revealed (kinetic decay of 671 nm signal, brilliant red line), with respect to the one of HgS pure sample (figure 1a, time profile of 670 nm signal brilliant red line).
In particular, figure 1d shows well-defined negative bands between 700 and 800 nm which can be ascribed to the presence of further trap centers due to the Cl^- ions in the structure. Even the UV treatment does not display an evident difference between doped (fig 1d) and undoped samples (fig 1b), except for a shortening of characteristic decay times of involved transitions.



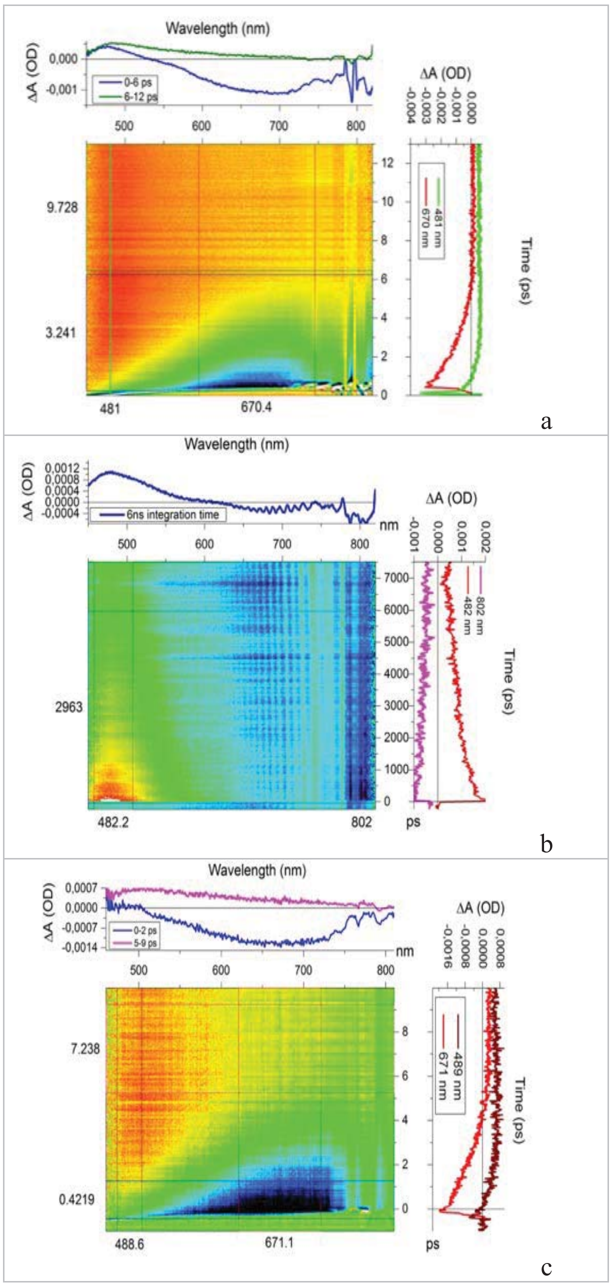
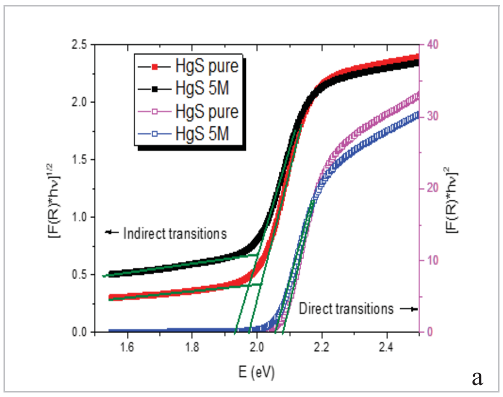


Fig. 1. TA maps of HgS before (a) and after UV exposure(b); and HgS-5MCl before(c) and after UV exposure(d).

In Fig. 2. we reported the direct and indirect transitions for all the samples. Upon UV irradiation, pure HgS transitions move from 2.05 eV to 1.92 eV for direct transitions and from 1.97 eV to 1.57 eV for indirect transitions. The HgS 5M sample changes the transitions from 2.08 eV to 2.01 eV (direct) and from 1.93 eV to 1.77 eV (indirect). These values are compatible with GSD signals obtained by the pump probe.
Therefore Tauc plots confirm the presence of alpha-cinnabar with a defective phase, but the formation of other chlorine-based compounds having a band gap over 2.0 eV seems to be ruled out, since all the mentioned possible Cl-related structures, corderoite, calomel, and mercury chloride, are endowed with higher values of the band gap.



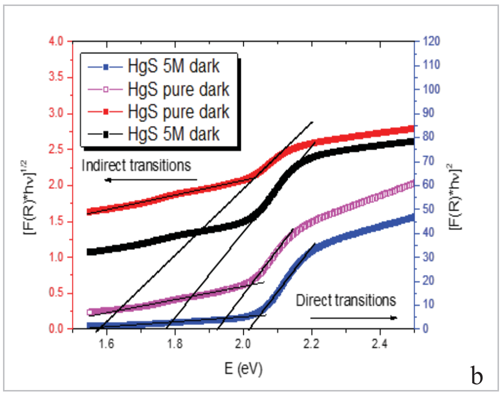
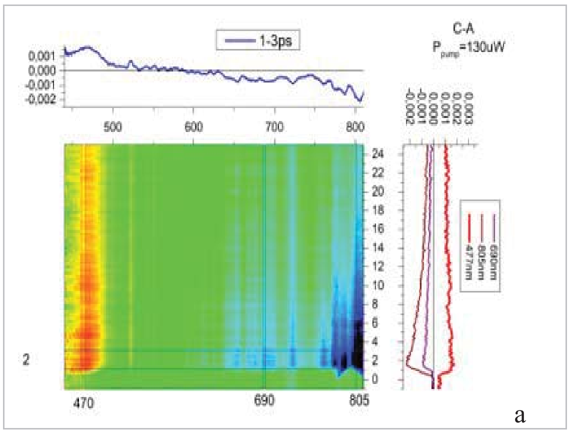


Fig. 2. Tauc Plots for Kubelka Munk function from Reflectance spectra of analyzed samples: direct and indirect transitions for pure and 5M HgS not exposed to UV light samples (a); direct and indirect transitions for UV exposed pure and 5M HgS samples (b).

B. Yellow and Orange cadmium pigments

In fig. 3. the transient absorption maps for all the cadmium samples, before and after the UV exposure, are reported. The substantial difference for the treated yellow samples (C-UV-56h) resides in the broadening of absorption signals (ESA), attributable to a change inside the conduction band structure, new levels due to the formation of defects, and changes in electronic transfer as suggested by different kinetics observed in some positive signals. For what concern the orange sample, the no-treated powder is composed of a long-live ESA signal centered at around 495nm. No negative signals were detected. The UV-exposed sample (S-UV-56h) showed variations in the kinetics of the ESA signal, that became shorter (duration of about 40 ps) and the formation of a new broad negative signal (ground state depletion) centered at 570nm towards trap states.



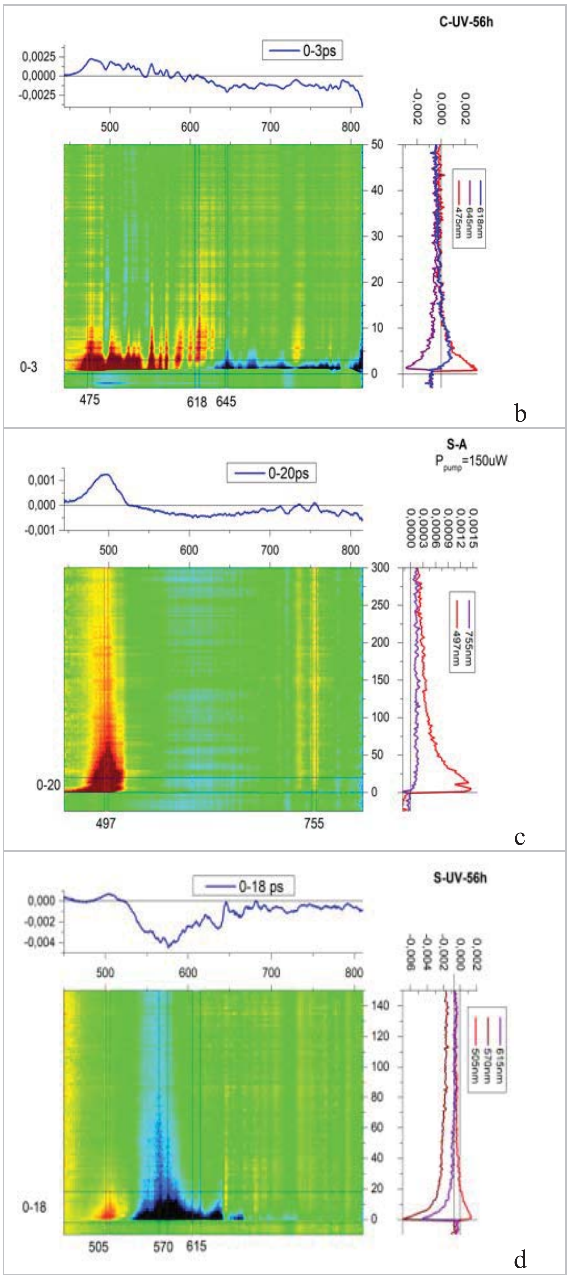


Fig. 3. a)TA maps of Cd-yellow no treated(C-A);b) TA maps of Cd-yellow after UV exposure (C-UV-56h);c) TA maps of Cd-orange no treated(S-A); d) TA maps of Cd-orange after UV exposure (S-UV-56h).

We can hypothesize that the negative signal in the NIR around 780 nm, found in both normal and UV-exposed samples, could be linked to Cd vacancies for the yellow sample. In the orange sample, the formation of new trap states inside the bandgap, are defects responsible for the change of color in aged samples.

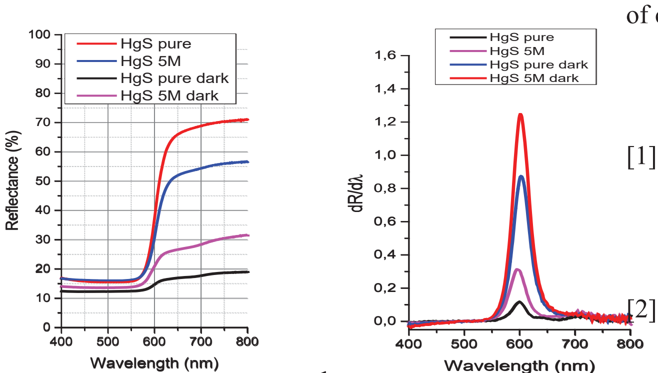
C. Colorimetric study

To have a complete characterization of the color variation, we performed a colorimetric study starting from the reflectance spectra. The colorimetric coordinates are reported in table 1.

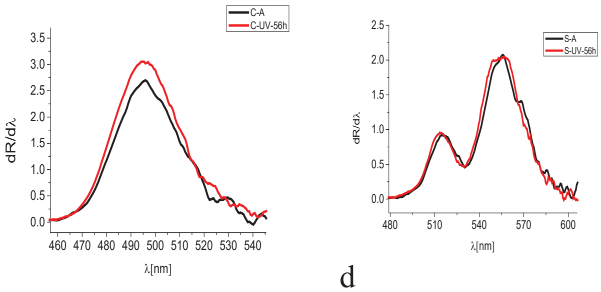
Table 1. Colorimetric coordinates for the analyzed samples before and after UV exposure.

	L	a	b
HgS pure	55	32	15
HgS pure UV	50	26	12
HgS 5MCl	53	24	10
HgS 5MCl UV	46	16	7.6
C-A	94	-11	75
C-A UV56h	99	-9	101
S-A	78	35	93
S-A UV56h	80	34	94

From these values, it is evident the variation of color properties due to the UV exposure that causes the famous effect of darkening in HgS samples, while in the case of Cd-yellow samples the variation of L and b coordinates is predominant for the C sample. In addition, with the help of derivative reflectance spectra (see figure 4b), in HgS samples after UV exposure (HgS pure UV and 5M UV) we notice the formation of two satellite bands at 650 nm and 730 nm compatible with the results obtained by transient absorption in regard to the formation of intra-gap levels due to the formation of trapping centers. For what concerns the Cd-yellow samples, derivative spectra do not present important variations confirming what is found with colorimetric coordinates.



a b



c d

Fig. 4. a)reflectance spectra of HgS samples after and before UV exposure; b) derivative spectra of Hgs samples; c) derivative reflectance of Cd-yellow sample C-A before and after UV-exposure(C-UV-56h); d) derivative reflectance of Cd-orange sample S-A before and after UV exposure (S-UV-56h).

IV. CONCLUSIONS

In summary, in this study, we analyzed the degradation of Red Vermilion, Cd yellow and orange standard pigments, with the purpose to provide useful information for the field of cultural heritage. The pigments were artificially degraded through UV light exposure. Although the orange pigment seems more stable, the yellow one degrades more markedly. In the case of Red Vermilion, the darkening effect is evident, especially in presence of Cl ions.

With the help of transient absorption measurements, we concentrate our attention on GSD and ESA signals for both pigments. We correlate them to the formation of trapping levels in the visible and near-infrared region both for HgS and CdS samples. The presence of these defects seems to generate the color variation registered from reflectance spectra and is evidenced in the variation of colorimetric coordinates.

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