SPECTROSCOPIC CHARACTERISATION OF LASER-INDUCED EFFECTS ON MODERN PAINT LAYERS

D. Ciofini *, S. Siano

*Istituto di Fisica Applicata "N. Carrara"-Consiglio Nazionale delle Ricerche (IFAC-CNR), Florence, Italy. d.ciofini@ifac.cnr.it

Keywords: laser, Vis-NIR PL, reflection, pigments, oil paint

Abstract

In this work, Vis-NIR steady-state photoluminescence (PL) emission and Vis-NIR reflection spectroscopy were used in order to investigate the effects induced on modern paint layers by LQS Nd:YAG(1064 nm) laser at subablative fluences. Cadmium yellow (Cdy), lithopone white (Liw) and chromium oxide green (Crg) pigments with and without oil matrix were investigated. The setup proposed allowed collecting reliable information on PL, color and morphology changes upon laser irradiation. Furthermore, the results achieved led to recognize, for the first time, the oil matrix alteration as the early trigger of the photothermal effects.

1 Introduction

There are a number of materials and irradiation features that influence the results and determine the side effects of the laser treatments in conservation of valuable artworks. This must be taken carefully into account especially when operating on painted artifacts. Firstly, the ablation mechanisms and the extension of photothermal, photochemical, and photomechanical effects strongly depend on the laser wavelength and pulsewidth. Secondly, the fluence, pulse repetition rate and irradiation condition (dry, gas, or liquid assisted), have to be suitably optimized for avoiding discoloration or other invasive effects [1],[2],[3]. To this purpose, electronic and vibrational spectroscopies have proved to be powerful non-destructive analytical techniques for assessing physicochemical modifications occurring on pigments, binders and their mixtures upon laser radiation [4],[5],[6]. Here, Vis-NIR steady-state PL emission, and Vis-NIR reflection spectroscopy were used in order to investigate the effects on modern paint layers induced by Nd:YAG (1064 nm) laser at subablative fluences. To this goal, a versatile setup, based on a
standard epi-fluorescence microscope equipped with a co-axial fiber optic spectrometer, monitor camera, and laser irradiation line was used in order to simultaneously collect fluorescence, color, and morphology information upon laser irradiation.

Materials and methods

1.1 Mock-ups preparation

Mock-ups were prepared using Liw, Cdy and Crg (supplied by Zecchi, Florence), which are inorganic modern pigments that slowly began to be used as artist paints in the mid-19th century, gaining in popularity in the early 20th century. These were mixed with boiled linseed oil containing Co-salts (0.05%) for speeding up drying and curing, and then applied on glass-slides and on primed linen canvas. Each paint layer was formulated with a pigment to binder (p/b) ratio of 65/35 wt%. Once dried to touch, a set of mock-ups was naturally aged (na) for an overall period of 4 years in controlled laboratory conditions (T=20°C, R.H. = 40-45%, E<150-200 lx) covered by 1 cm thick of polymethyl methacrylate (PMMA), which acted as a UV filter cutting wavelengths below 380 nm. A further set of mock-ups was instead artificially aged (aa) under six OSRAM DULUX+ 55W/954 daylight fluorescent tubes (5400 K color temperature) by filtering with the mentioned PMMA UV filter in order to simulate the museum conditions. During the experiment, the illuminance measured at sample surface by means of a digital photometer (probe precision: ±5%) was 15.6 klx ±0.3. The total exposure time, corresponding to 2700 hours, may be calculated, assuming reciprocity, to be equivalent to about 70 years of exhibition in recommended museum conditions (200 lux eight hours/day).

Pressed pellets of pigment and oil film were also independently investigated in order to discriminate the respective contribution to the PL signal. Pellets were prepared using 0.5 g of pigment powder pressed for 5 minutes at 150 bar.

1.2 Laser irradiation tests

Laser irradiation tests were performed using a fiber coupled (600 μm core diameter) LQS Nd:YAG(1064 nm) laser emitting pulses of 120 ns and energy of 120 mJ/pulse. The laser beam was aligned along the microscope optical axis using a dichroic mirror mounted at 45° in place of the microscope’s objective lens. To study the subablatve effects, samples were irradiated using fluences of 0.5-0.4 times smaller than the ablation fluence thresholds, $F_{th}$, as measured on the single-shot basis [1]. A maximum number of 100 laser pulses was delivered at each irradiation location by using dry condition, fixed spot diameter of 3 mm and 1 Hz pulse repetition frequency. LabMax-TOP, Coherent Inc., power meter and suited neutral density filters were used to finely set the laser fluence. The optical parameters at 1064 nm of the oil paint layers were measured through reflectance ($R$) and transmittance ($T$) measurements using an integrating sphere. The optical penetration depth ($\delta$) was then derived on pigment-oil mixtures following a well-established procedure reported elsewhere [7].
1.3 Vis-NIR steady-state PL

A high-sensitivity Avantes ( AvaSpec) CCD spectrophotometer (200–1100 nm, grating 300 lines/mm) was coupled via 200 µm core quartz optical fiber to an epi-fluorescence microscope (Nikon Eclipse 400) equipped with HBO mercury short-arc lamp (emission above 295 nm). To excite and collect PL emission a V2A filter cube (Exc.: 380-420 nm. DM: 420 nm, Bar.: 450 nm) provided by Nikon was used. The excitation light was focused onto the sample surface using a 20x Plan Fluor objective lens (field of view 1 mm) and the PL emission was then collected by a lens with focal length of 20 cm and sent to the spectrophotometer via optical fiber. The response of the spectrometer was calibrated over the whole spectral range using a light-CAL source. In this way, the intensities of the PL spectra were made comparable, taking into account that the PL intensity depends on the incident irradiance, amount of fluorophores, fluorescence quantum yield (QY) of each fluorophore, and sample homogeneity. For avoiding any shortcomings (i.e. self-quenching) induced by the HBO lamp during PL acquisition, a linear domain where the PL intensity remained unvaried over the measuring time was found for each set of samples. The power output from HBO lamp was measured using a fast (4 ns of rise time) silicon photodiode. The measured output, using ND filters, ranged between 1-15 mW/cm². This early calibration allowed to detect the laser-induced effects independently from possible shortcomings ascribed to power density of the HBO lamp. The optimal measuring conditions were achieved by averaging three acquisitions of 500 ms integration time. Fluorescence variations following laser irradiation are expressed as PL intensity (PLI) ratio between laser-irradiated and non-irradiated area.

1.4 Vis-NIR reflection and colorimetry

Vis-NIR reflection and colorimetric parameters were acquired through the setup described above, although in this case the light source was positioned at 45° with respect to the surface of the sample (i.e. specular component excluded). The light source used was a stabilized 10W Tungsten halogen lamp (Illuminant A), fan cooled, coupled to a fiber bundle (6×200 µm core fibers). Vis-NIR reflection spectra were collected, as for PL, between 450-1100 nm while colorimetry was carried out within the standard spectral range 380-780 nm. For both cases, an integration time of 500 ms and averages of 5 measurements were used. L*a*b* parameters, as well as Hue angle, Chroma and color variation (ΔE), have been calculated using CIELab76 color space and 2 degrees standard observer. Calibration was performed by means of 99% Spectralon diffuse reflection standard. Colorimetric differences before and after laser irradiation (ΔL*, Δa*, Δb*, Δh*, ΔC*, ΔE) were hence determined.
2 Results and discussion

2.1 Samples characterization

Vis-NIR PL and reflectance spectra of Cdy, Liw and Crg samples are displayed in Fig.1.

![Fig. 1 Vis-NIR PL (solid lines, left Y-axis) and reflection (dashed lines, right Y-axis) of Cdy (a), Liw (b) and Crg (c) samples. na: naturally aged. aa: artificially aged.](image)

Cdy-pellet had a broad PL emission in the 700-900 nm range with $\lambda_{\text{max}}$ at about 790 nm, two marked shoulders at 720 and 860 nm and a weak PL tail up to 1000 nm. This red-near infrared emission bands are generally assigned in Cd-based pigments to lattice defects, impurity ions and sulfur vacancies which generate deep-trapping states below the conduction band [8]. However,
PL band at 790 nm (1.57 eV) is assigned to deep- level emission of hexagonal-CdS, while the shoulder at 860 nm and weak PL around 1000 nm are attributable to CdSSe (increasing amount of Se produces red-shifting), although both Zn and Se were detected in ESEM-EDX analyses. The very weak and double-structured band-edge emissions around 510 nm (2.43 eV) and 518 nm (2.39 eV), are ascribed to the presence of both hexagonal and cubic CdS phases, respectively [9]. These barely distinguishable peaks are no longer detectable in complex oily matrices [10]. Spectra of Cdy-oil (na and aa) paints also showed a further intense peak at 545 nm attributable to the linseed oil fluorescence, which was more pronounced for na sample than aa. This contribution was also observed in Liw and Crg oil mixtures. PL emission $\lambda_{\text{max}}$ of Liw-pellet, Liw-oil_na and Liw-oil_aa were detected at 465, 475 and 480 nm, respectively. It should be noted that, when in mixture with oil, the PL emission was shifted and enhanced of almost one order of magnitude with respect to the pellet (Fig.1b). Conversely, Crg-pellet did not exhibit fluorescence peaks at the present excitation wavelengths, whereas for both na and aa oil paints a green band ($\lambda_{\text{max}}$ at 525 nm) was detected. The latter is red- shifted with respect to that of the (one-month old) oil binder at 460 nm (spectrum not shown).

As regards reflectance spectra, Cdy samples showed a very high NIR reflectance (85% at 1064 nm) and the typical S-type band shape of Cd (S, Se) semiconductors. A closer inspection of Cdy-pellet spectrum between 650-800 nm revealed the presence of ZnS, thus confirming what previously inferred by PL spectra and ESEM-EDX. With respect to Cdy-oil_na sample, reflection in Cdy-oil_aa appeared to be slightly smaller in the 600-1100 nm range. Liw-pellet (ZnS + BaSO$_4$) was characterised by its well-known reflectance profile. BaSO$_4$ is one of the compounds presenting the highest reflectivity (>98%) over the UV-Vis-NIR (250-2500 nm) spectral range, while the rather broad absorption between 650-800 nm is assigned to Co$^{2+}$ ion in tetrahedral coordination with ZnS [11]. However, Liw-oil paint layers (na and aa) exhibited lower reflectance as compared to Liw-pellet. Lastly, Crg-pellet (Cr$_2$O$_3$) and related oil mixtures are characterised by a green reflectance peak at about 550 nm and a broad band over the NIR window. At 1064 nm the reflectances of the present samples were about 18% and 25% for pellet and paint layer, respectively.

2.2 Laser irradiation tests

Laser irradiation of the paint mock-ups along with fluorescence, color, and morphology characterizations carried out as function of laser pulses (max. 100 per spot) at subablative fluences ($F=0.5 \, F_\text{th}$), have provided the basis to discuss the different induced effects. The results achieved are plotted in Fig. 2. As shown, very interestingly, the PLI ratios and all the calculated color parameters in Cdy and Liw pellets remained practically unvaried with increasing laser pulses. Similarly, no side effects (discoloration, PL quenching) were observed for naturally and artificially aged Liw-oil mixtures. In contrast, irradiation of Cdy-oil samples produced a dotted alteration pattern where small dark spots of 2-10 µm size increased randomly in number with delivered laser pulses until getting a homogeneous distribution within the irradiated area. This led to an overall decreasing of
15-20% in the PLI ratio of oil component, which is reflected also in that of the pigment. It should be stated that the cause of this effect cannot be related properly to a PL quenching, neither of the matrix or of the deep-level PL bands of the Cdy, but rather to the onset of thermal alteration associated with microscale photo-mechanical detachments. In fact, closer inspection either with optical and electron scanning microscopes, revealed the presence of micro-alterations and- cratering on the paint surface, which most likely acted as optical traps for the PL signal. Consequently, overall decreases of $\Delta L^*$, $\Delta a^*$, $\Delta b^*$, and $\Delta C^*$ were recorded. This effect was more pronounced in the na than in aa samples. In fact, the former exhibited the highest color change ($\Delta E=16$) measured, while for the latter the $\Delta E$ after 100 pulses was about 8. With respect to Crg-pellet, though not luminescent, $\Delta h^*$ increased and $\Delta L^*$ decreased as consequence of a surface texturing effect due to cumulative heating. Likewise, PL emission ascribed to oil binder in Crg-oil paint film was slightly quenched (15 %) with the number of laser pulses. In this case, Crg pigment acted as PL quencher for the oil matrix. The color change was instead mainly ascribed to the whitening/swelling (increase of $\Delta L^*$) of oil matrix.

To summarize, the samples studied showed different behaviors upon laser radiation at subablative fluences. Cdy, Liw, and Crg pellets resulted very stable, as no thermal side effects, PL quenching, or discoloration were observed. Similarly, Liw-oil was insusceptible to laser radiation ($R=73\%, \delta=67 \mu m$), while Crg-oil ($R=21\%, \delta=12.4 \mu m$) underwent a slight PL quenching of the oil binder mainly induced by the heating of the pigment. Similarly, the PLI ratio in Cdy-oil paint ($R=85\%, \delta=70 \mu m$) dropped down due to the accumulation of surface micro- alterations. This phenomenon led also to a corresponding higher color variation ($\Delta E=16$). The spectroscopic results along with microscope inspections suggest the nature and the extent of this phenomenon may mostly depend on the degree of polymerization of oil binder, presence of paint film defects, and/or nano-absorbing impurities within the crystal lattice of CdS.

3 Conclusions

The present work proposes a reliable methodology for assessing laser-induced physicochemical effects on paint layers at subablative fluences. The results achieved allowed to discriminate, for the first time, the oil matrix alteration as the early trigger of the undesired irradiation effects. No detrimental evidences were pointed out for Liw and Crg-based pellets and oil paints, which allows foreseeing a corresponding promising application perspective of the laser uncovering. Conversely, the pronounced photosensitivity of Cdy-oil paint films implies more strict limitations in laser treatments, which should be tested and applied only under strict control of the irradiation parameters and conditions. Further studies will be dedicated to investigate in depth the nature of the observed subablative effects in Cdy-oil paint layers.
Fig. 2 PLI ratios (a-c) and color parameters variation (d-i) measured at sub-ablative fluences (F=0.5 $F_{\text{th}}$) on Cdy, Liw and Crg oil-based paint layers.

Acknowledgments

The present work was supported by IPERION-CH “Integrated Platform for the European Research Infrastructure on Cultural Heritage” (H2020, INFRAIA 2014-2015, Grant no. 654028).

References

[1] S. Siano, I. Osticioli, A. Pavia, and D. Ciofini, “Overpaint removal from easel paintings using an LQS Nd: YAG laser: The first validation study,” Stud. Conserv., vol. 60, no. S1, pp. 49–57, 2015.

[2] S. Siano, M. Giamello, L. Bartoli, A. Mencaglia, V. Parfenov, and Salimbeni, “Laser cleaning of stone by different laser pulse duration and wavelength,” Laser Phys., vol. 18, no. 1, pp. 27–36, 2008.

[3] R. Salimbeni, R. Pini, and S. Siano, “A variable pulse width Nd:YAG laser for conservation,” J. Cult. Herit., vol. 4, pp. 72–76, 2003.

[4] M. Oujja, M. Sanz, E. Rebollar, J. F. Marco, C. Domingo, P. Pouli, Kogou, C. Fotakis, and M. Castillejo, “Wavelength and pulse duration effects on laser induced changes on raw pigments used in
paintings,” *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 102, pp. 7–14, 2013.

[5] M. Chappé, J. Hildenhagen, K. Dickmann, and M. Bredol, “Laser irradiation of medieval pigments at IR, VIS and UV wavelengths,” *J. Cult. Herit.*, vol. 4, pp. 264–270, 2003.

[6] D. Ciofini, M. Oujja, M. V. Cañamares, S. Siano, and M. Castillejo, “Spectroscopic assessment of the UV laser removal of varnishes from painted surfaces,” *Microchem. J.*, vol. 124, pp. 792–803, 2016.

[7] D. Ciofini, I. Osticioli, a. Pavia, and S. Siano, “Removal of overpaintings from easel paintings using LQS Nd:YAG laser,” *Appl. Phys. A*, vol. 117, no. 1, pp. 341–346, 2014.

[8] O. O. Artem, O. V Vakulenko, and O. I. Dueniko, “Amphoteric center of luminescence in CdS,” no. 11, pp. 58–60, 2005.

[9] V. Babentsov, J. Riegler, J. Schneider, M. Fiederle, and T. Nann, “Excitation dependence of steady-state photoluminescence in CdSe nanocrystal films,” *J. Phys. Chem. B*, vol. 109, no. 32, pp. 15349– 15354, 2005.

[10] M. Thoury, J. K. Delaney, E. R. De La Rie, M. Palmer, K. Morales, and J. Krueger, “Near-infrared luminescence of cadmium pigments: In situ identification and mapping in paintings,” *Appl. Spectrosc.*, vol. 65, no. 8, pp. 939–951, 2011.

[11] H. a. Weakliem, “Optical Spectra of Ni$^{2+}$, Co$^{2+}$, and Cu$^{2+}$ in Tetrahedral Sites in Crystals,” *J. Chem. Phys.*, vol. 36, no. 8, pp. 2117–2140, 1962.