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Photoluminescence properties of zinc white

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Summary. — Zinc white pigment has characterized artist's palettes from the end of the eighteenth century up the twentieth century. It thus belongs to the modern pigments which were industrially produced by inorganic material (ZnO). This new category of pictorial materials interested conservators and scientists mainly for its behavour with aging. For this reason, this work focuses on the understanding of photo-physical behaviour of zinc white based on a time-resolved analysis of photoluminescence emission of historical samples. This study allowed the characterization of the decay kinetic properties of photoluminescence emissions. All historical samples showed near-band-edge and trap state emissions, typically occurring in semiconductors, that were modified by the interaction of the pigment with the surrounding organic binding material. The study further suggests that zinc carboxylates, detected in all historical samples, could be responsible for changes in emission mechanisms. Generally, data demonstrates how time-resolved photoluminescence spectroscopy is a powerful method for elucidating the nature of the mechanism processes in luminescent semiconductor pigments.

1. – Introduction

The development of new scientific technology has given new insight into the conservation and preservation of cultural heritage. As an example, techniques such as X-Ray fluorescence (XFR) for elemental detection or Raman spectroscopy for molecular characterization are widely applied as preliminary analyses on paintings [1]. Such methodologies based on characterization of materials have the advantages of being non destructive and at the same time able to provide useful information, sometimes resolutive for historical questions [2]. One of the most significant issues for museum curators is related to conservation of modern paintings. This necessity is strictly connected to the material used by artists in the last century *i.e.* pigments produced industrially from inorganic materials. Modern pigments became attractive thanks to their beautiful texture and colour and they rapidly substitute the previously used organic and inorganic pigments. Degradation processes related to modern pigments are diverse and not negligible since

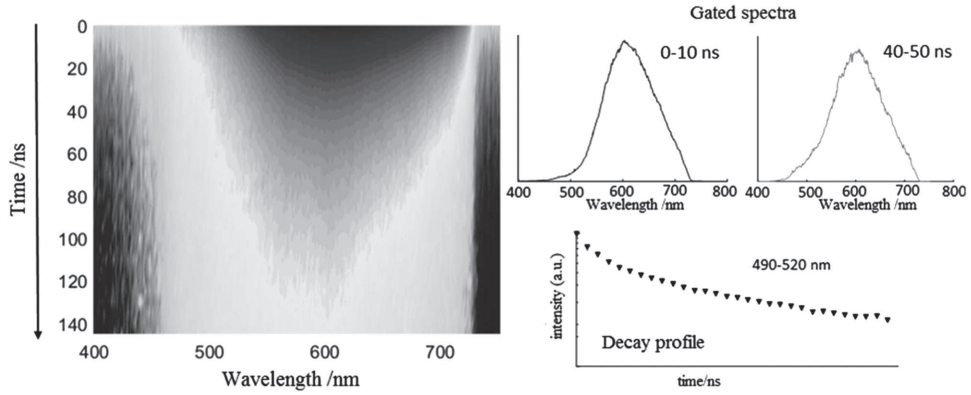

Fig. 1. – Data matrix obtained from a Time-Resolved Photoluminescence (TRPL) spectroscopy. On the horizontal axis is shown the wavelength (nm), whereas on the vertical axix the time (ns/ μs). The false colour scale represents the relative intensity. Fixing time region, the obtained spectrum is the gated spectrum. Fixing wavelength region, the intensity dependence on time is the decay profile.

modern paintings may rapidly deteriorate and colour-fading of the painted surface may occur [3].

Zinc white belongs to this modern pigment group and it became the predominant white pigment from the beginning of the 20th century. Since it was obtained as final material from zinc oxide burning, it presents most of the optical feature of the semiconductor material ZnO and for this reason usually one refers to it as a semiconductor pigment [4]. At present, zinc white is no longer used by artists because of its rapid degradation processes especially when mixed with organic binder that lead to cracking and yellowing of the white paint [5]. Because of increasing interest in photo-physical behaviour of zinc white, we performed photoluminescence characterization of historical pastels based on zinc white using a time-resolved spectroscopy. This method allowed the determination of typical photoluminescence spectrum of historical samples of zinc white and the characterization of the recombination dynamics.

2. – Materials and methods

As case of study, twelve fragments of historical pastels based on zinc white were selected. This set of samples belongs to a collection of LeFranc Bourgeois from the beginning of the twentieth century. Since zinc white is mainly composed by zinc oxide (specifically in selected samples other compounds were found as traces materials or due to colourant in pastel itself), it is characterized by photoluminescence properties of semiconductor of the II-VI group [6]. In fact, zinc oxide has a large band gap (3.4 eV) and a direct transition due to band-to-band recombination (BE) that stimulated with UV light emits a narrow band around 370 nm. In addition, defects and impurities of the crystalline structure lead to the presence of intra-band energetic levels that act as trap state levels (TS) which have longer recombination lifetimes (lower recombination probability) that usually occur in the visible region [7]. The different origin of the two recombination paths and thus the different lifetimes gave support to the application of a time-resolved spectroscopy technique to analyze such samples [8].

The time-resolved spectrometer used to detect the photoluminescence properties of zinc white is based on a nanosecond pulsed laser (Q-switching Nd:YAG laser) at 355 nm as stimulation source. The maximum pulsed energy is 70 μJ with a pulsed duration of 1.0 ns and a repetition rate of 100 Hz. This allows zinc oxide to be first stimulated and and then to relax to its ground-state level, since the time required by trap state level to recombine is of order of 5 μs. The pulsed laser is injected into a fiber and with an optical system, it is focused onto the sample with a circular spot of 1 mm as diameter. In back-scattering geometry, the photoluminescence emitted by the sample is collected and focused into a spectrometer (150 lpmm grating) which is able to select wavelength between 380–700 nm and has a spectral resolution of 5 nm. The spectrometer is coupled to a gated intensifier and a CCD camera. This final set up is capable to select the emitted photoluminescence at different selected time delay and with different gate window that allows the detection of prompt luminescence (nanosecond) or delayed luminescence (microsecond). An example of obtained data is presented in fig. 1. The matrix can be read horizontally, fixing time and having information about the spectrum emitted at some delay. Alternatively, fixing the range of wavelength, the specific emission changes in intensity with time, *i.e.* the decay profile, can be read. The evaluation of lifetime of different recombination path was done by interpolating the decay curve with a tri-exponential function [9]:

$$I(t) = \Sigma_i A_i \tau_i \left(1 - e^{-w/\tau_i}\right) e^{-t/\tau_i}, \tag{1}$$

where w is the chosen gate window, τ_i is the i-th constant decay component, A_i is the weight of the i-th component and t is time on which the intensity (I) depends. The effective lifetime used to evaluate differences between samples is calculated

$$\tau_{ef} = \frac{\Sigma_i A_i \tau_i^2}{\Sigma_i A_i \tau_i}. \tag{2}$$

3. – Results and discussion

Time-Resolved Photoluminescence (TRPL) analysis was applied on twelve historical pastels based on zinc white [10]. Despite different colour and different traces elements, a great accordance (σ less than 15%) was found looking both at spectrum and decay profile. The narrow emission at approximately 390 nm confirmed the presence of zinc oxide as main the compound of zinc white, while the emission from trap state levels showed a broad emission centered in the green (at 530 nm) but covering nearly the whole visible region, from 450 to 750 nm (fig. 2). For the time-resolved analysis, the time zero was fixed at t^* that corresponds to the maximum of the pulsed laser, after which the recorded luminescence is only representative of BE recombination. The decay profile of BE emission from 0 to 30 ns and the decay profile of TS emission from 1 to 15 μs were interpolated with two and three exponential fitting (eq. (1), eq. (2)), respectively. The numerical results for the historical samples are reported in table I and their average value is compared with the effective lifetime of a commercial zinc white powder (Kremer pigmente GmbH) used as reference sample. The good agreement between historical samples is in contrast with a discordance with the result obtained from the reference sample. Such difference may be considered as a proof that photoluminescence properties of zinc white changes if it is mixed with organic binders (wax and linseed oil were detected in pastel samples).

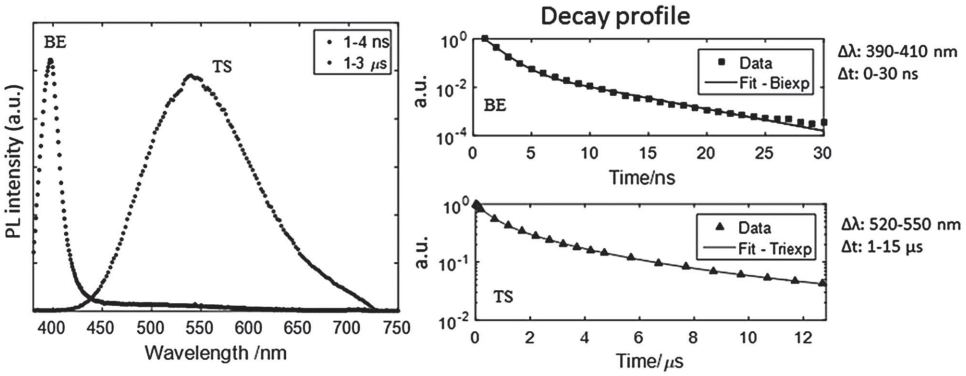

Fig. 2. – On the left: the PL gated spectra for BE and TS emissions. On the right: an example for the decay profile for both emissions interpolated with eq. (1).

With the aim of material characterization, the effect of fluence (defined as energy impinging onto the sample per unit of surface, $\mu\,\mathrm{J/cm^2}$) on photoluminescence intensity was evaluated. By varying the fluence between the maximum allowed by the laser and decreasing it by the mean of neutral optical density, the intensity of BE and TS emission peak was detected. Referring to fig. 3, the two emissions seem to both have a linear dependence on fluence, but at the lowest fluence the emissions have a different shape. First, the BE emission increases faster at low fluence, becoming linear at high fluence. TS emission is much less intense than BE emission and increases slower with increasing of fluence. In general, both emissions can be interpolated with a power function of the fluence, as $I \sim F^k$, where I indicates the photoluminescence intensity, F the fluence and k is a constant. From semiconductor theory [11], it is known that semiconductor material has similar dependence and in particular, when k is greater that one ($k_{BE} = 1.28$), the recombination is associated with an exciton-like transition, while when k is less than one ($k_{TS} = 0.70$) the recombination is related to a free-to-bound or donor-acceptor transition (table II). At low fluence (low number of impinging photons) the system recombines through direct recombination and relaxes also via trap state levels. On the other hand, increasing fluence (high number of photons) the trap state levels saturate and the favoured recombination path is the direct one. Note, finally, that usually the boundary value of k equal to one is usually associated with direct recombination. In this way, the detected peak at 390 nm is not truly associated to a direct BE emission but to a near-band-edge recombination, which explains the higher wavelength value of the peak with respect to the one expected for ZnO (around 370 nm).

Possibly, the detected changes between results from historical samples and zinc white

TABLE I. – *Average effective lifetime obtained for BE and TS emission from twelve historical pastel samples. The results are compared with the effective lifetime from a reference zinc white sample.*

	τ_{ef}: BE	τ_{ef}: TS
Historical samples	1.31 ns ($\sigma = 0.20$ ns)	3.26 μs ($\sigma = 0.60$ μs)
Reference zinc white	0.55 ns	5.27 μs

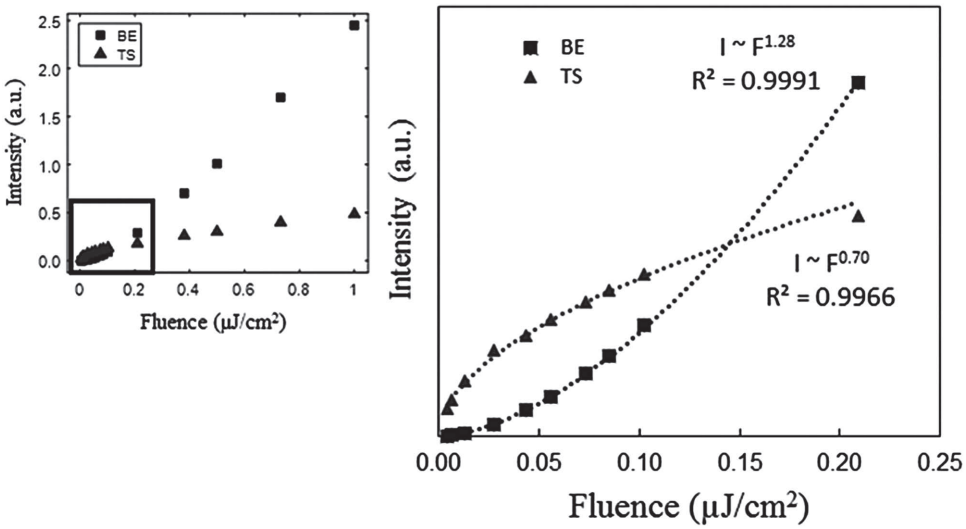

Fig. 3. – Emission intensity dependence on fluence (μ J/cm^2). The BE data is reported with the square, whereas the triangle indicates the TS data. On the right the blown-up inset at low fluence from which is clearly visible the power dependence of the intensity on the fluence: $I \sim F^k$.

powder in both effective lifetime and dependence on fluence are caused by the interaction of the pigment with the organic binder [12]. One should bear in mind that the selected historical samples are made by complex matrix of ZnO, additives (coloured pigments), binders (wax and linseed oil) and finally degradation products. Indeed, FTIR spectroscopy applied on historical samples revealed the presence of zinc carboxylates formed after the reaction of free fatty acids of oleic binder and metal ion of pigment (in this case Zn) [13]. The final formed cluster, that increases in size with progressive aging, are called zinc soaps and at present strong effort is made in understanding their chemical evolution [14]. The question is now how this complex environment affects the photoluminescence properties of modern pigments, and in particular of zinc white. As a test, zinc white powder was mixed with two different organic binders, linseed oil and arabic gum. The TRPL analysis on these mock-up samples open new perspectives for understanding pigment-binder interaction. Results obtained from this test were the enhancement of PL emission in the blue region, change in lifetime of green emission (530 nm) and an increase in the effective lifetime of BE emission. At this stage, no straightforward explanation of these effects could be advanced. However this test encourages future studies since the results are in accordance with those obtained in historical pastels.

TABLE II. – *Average k value obtained for BE and TS emission from twelve historical pastel samples. The results are compared with the k value from a reference zinc white sample.*

	k: BE	k: TS
Historical samples	1.28 ($\sigma = 0.09$)	0.70 ($\sigma = 0.04$)
Reference zinc white	1.58	0.54

4. – Conclusion

The time-resolved spectroscopy was applied to obtain insights on the photoluminescence properties of zinc white. Results show that zinc white pigment behaves as a semiconductor, it is characterized by a short- and a long-living photoluminescence emission due to near-band edge and trap state recombinations. However, differences detected between historical samples and zinc white demonstrate that the organic environment introduced by the binder presence cause changes in the photo-physical properties of such semiconductor pigment. More work is needed to understand the reason for the variation in the lifetime of emissions in zinc white when mixed with binders. In general, time-resolved photoluminescence could become a valuable non-invasive tool to study the degradation of modern pigments.

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