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Photoluminescence Spectroscopy of ZnO and TiO_2 Pigments

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In the late 19th and early 20th century zinc oxide (ZnO) became available as an inexpensive alternative to lead white [2 $PbCO_3 \cdot Pb(OH)_2$] as a white pigment. However, poor chemical and mechanical properties for ZnO pigments have proved problematic in the field of painting conservation, as a result, TiO_2 has supplanted ZnO white given its superior opacity and greater chemical stability in paints [1]. The development of additional noncontact and nondestructive methods for identifying ZnO and TiO_2 in historical paintings that may contain mixtures of the two pigments is of clear value. Recently, time-resolved photoluminescence (PL) spectroscopy and microscopy has shown promise for understanding incipient alteration of ZnO in paintings [2,3]. Here we demonstrate that two-photon fluorescence lifetime imaging (FLIM) over selective spectral regions provides an additional novel method for the discrimination between these two white pigments in a painting cross section.

FLIM images were acquired using a NIST-built two-photon microscope. The sample was excited using a femtosecond Ti:sapphire laser centered at 750 nm with a repetition rate of 20 MHz to provide a sufficient time window for longer lifetime PL processes. The laser was focused onto the sample using a high numerical aperture air objective (0.95 NA) with a lateral resolution of ≈400 nm. Images were acquired by rastering the sample using a piezo scan-stage. The resulting PL was collected using the same objective and sent a detector for time-correlated single photon counting. Photon arrival time histograms were collected at each pixel and fit to create lifetime images. X-ray imagery was collected with an FEI Apreo SEM operated at 9 kV in variable pressure mode (P_{H20}=50 Pa) using dual Bruker XFlash 6|60 silicon drift detectors [4].

PL spectra for pigment separates (ZnO, and TiO_2) and a paint filler ($CaCO_3$) are shown in Figure 1a. ZnO exhibits strong luminescence in the UV, which can be exploited to identify ZnO in the presence of other pigments and fillers. In addition to the spectral specificity, the lifetime characteristics also provide a fingerprint. Figure 1b shows histograms of the weighted average lifetime in the 400 nm-410 nm spectral region. ZnO PL is the dominant signal in this wavelength range. The TiO_2 is several orders of magnitude weaker and has a shorter lifetime in this band, while $CaCO_3$ lifetime data was not detectable. This indicates the separates can be identified using lifetime in this spectral region. As a result, FLIM provides a straight forward approach for identifying ZnO and TiO_2 in paintings. To evaluate the discriminating capability of PL, we acquired a FLIM image of a painting cross section (Fig. 2a,b) with long-lived ZnO luminescence represented in orange and short-lived TiO_2 luminescence in blue. The 400 nm-410 nm FLIM and Zn, Ti, and Ca x-ray imagery are well correlated for ZnO in the light blue layer, and TiO_2 in the white paint layer. As expected, $CaCO_3$ is non-luminescent in this spectral band. $BaSO_4$ also used as filler material, is also non-luminescent in the 400 nm-410 nm region (Fig. 2 b,c). These results demonstrate that FLIM is an additional non-destructive method to identify ZnO, TiO_2, and potentially a number of other pigments at sub-micron resolution in complex materials such as paintings.

References:
[1] H. Kuhn in “Artists’ Pigments”, ed. R.L. Feller, (1986, National Gallery of Art), p169-186.
[2] A. Artesani et al., Appl. Phys. A **122** (2016), p. 1053.
[3] A. Artesani et al., Materials **10** (2017), p. 340.
[4] Any mention of commercial products is for information only; it does not imply recommendation or endorsement by NIST.

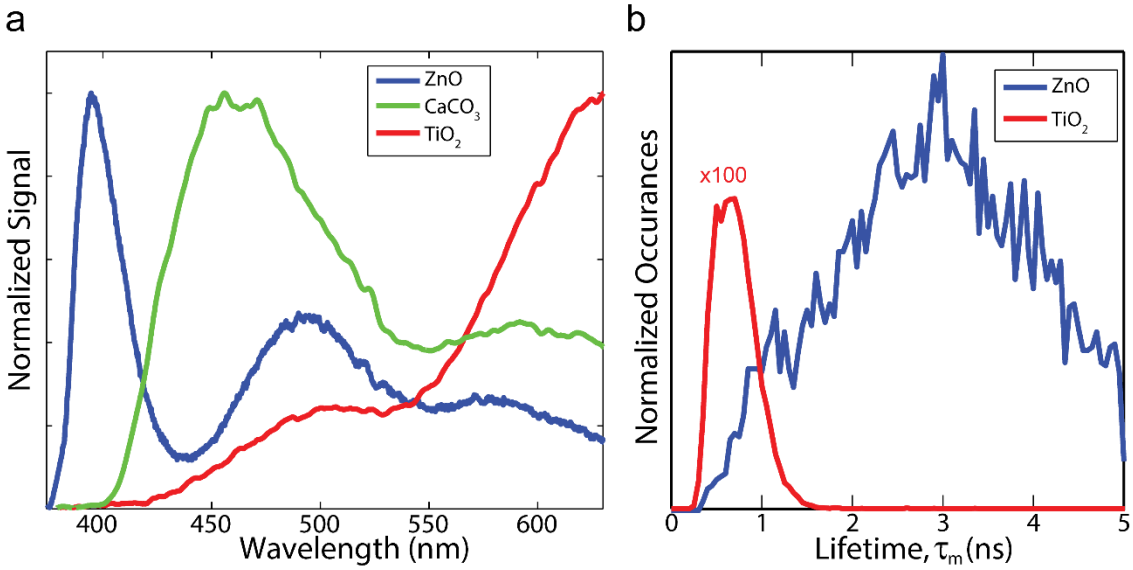

Figure 1. Spectra for separates of ZnO, TiO2, and $CaCO_3$. a) Luminescence spectra of ZnO (blue), $CaCO_3$ (green), and TiO_2 (red). b) Histograms of the average lifetimes for ZnO (blue) and TiO_2 (red) for 400 nm-410 nm. Histogram for TiO_2 is scaled up by a factor 100. $CaCO_3$ was not detectable.

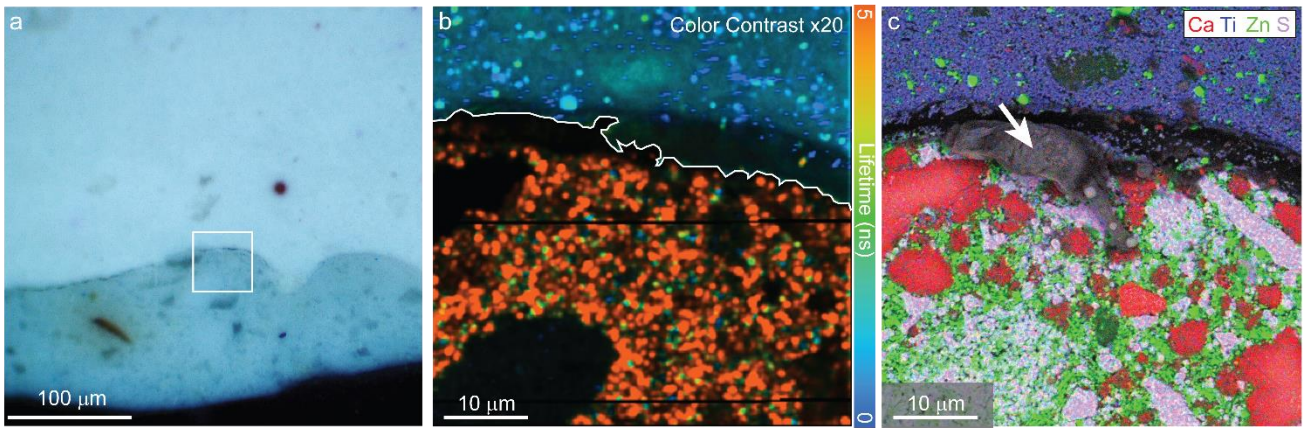

Figure 2. Painting cross-section at a layer interface. a) White light image where white square indicates the FLIM and EDS region of interest at the interface between light blue and white layers. b) FLIM image for 400 nm-410 nm luminescence. Orange represents ZnO and blue represents TiO_2. Color contrast for the white region is scaled up by a factor of 20 for visualization. c) Composite x-ray image superimposed on a backscattered electron image of the same region [Ca (red), Ti (blue), Zn (green), and S (lavender)]. White arrow highlights C-rich film likely associated with varnish likely related to a previous painting surface.