Supplementary Materials

Experimental study on the link between optical emission, crystal defects and photocatalytic activity of artist pigments based on zinc oxide

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Material Characterisation

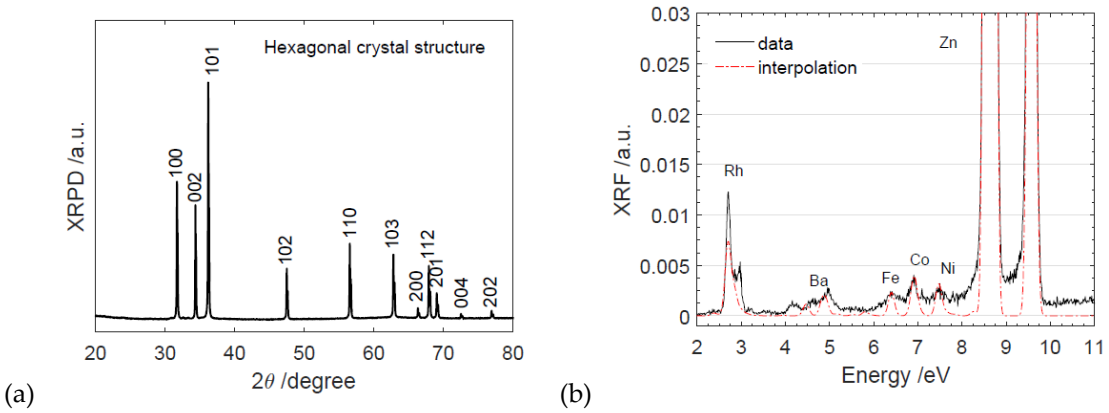


Figure S1 – All samples have the same diffraction pattern and metal impurities. **(a)** Hexagonal pattern of ZW1 is shown, with the highest diffraction peak associated to the (101), (100) and (002) crystal face. Identical pattern is found for the other samples. **(b)** X-Ray Fluorescence spectrum. The techniques identify in addition to Zn, other metal impurities which are easily included in the zinc oxide structure.

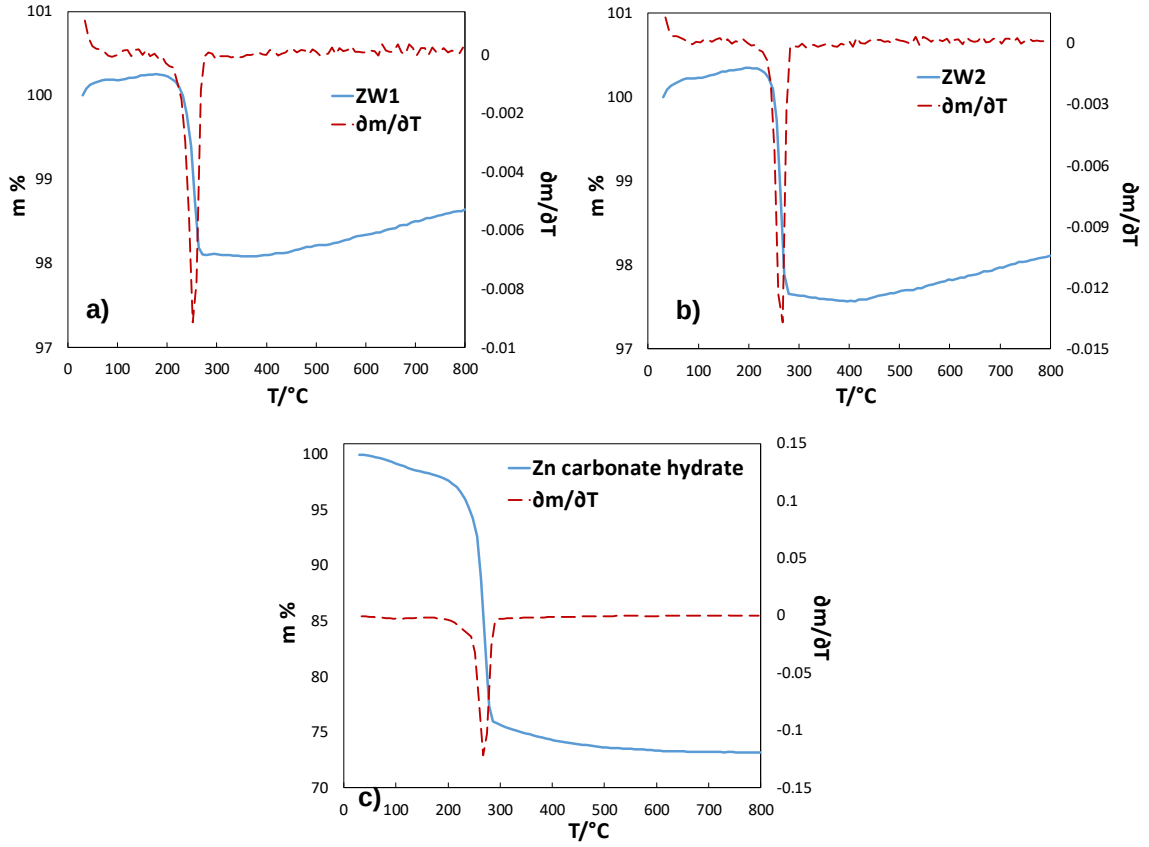


Figure S2 - Thermogravimetric analyses carried out between 30 and 800 °C, with heating ramp of 10 °C min^{-1}, in a 50 mL min^{-1} air flux for ZW1 (a) and ZW2 (b) samples. The TGA profiles (blue color) together with the calculated derivates (red color), i.e. defined as δm/δT. Data obtained with pure Zinc Carbonate Hydroxide are also reported for comparison **(c)**.

Crystalline Defects and Optical Emission

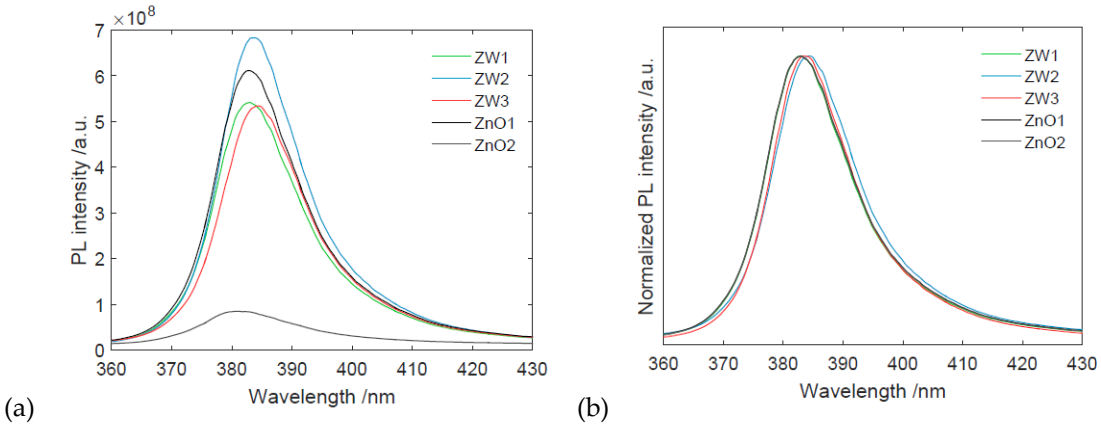


Figure S3 - **(a)** Near-band-edge emission of zinc white and zinc oxide samples, acquired with a gate window of 5 ns and delay of 0 ns. **(b)** Normalized spectra at the emission maximum, for comparing the peak position and the shape of the emission.

Table S1 - Results of analysis of near-band-edge emission decay kinetic fitted with a two-exponential decay model [17]. Here the single lifetime (τ) and the relative weight (A%) are reported. Values are given for all studied samples for the NBE emission integrated in the 370-410 nm region.

Near-Band-Edge Luminescence					
	A1 (%)	A2 (%)	$\tau 1$ [ns]	$\tau 2$ [ns]	$\bar{\tau}$ [ns]
ZW1	97.6	2.3	1.1	4.6	1.4
ZW2	96.0	4.0	1.2	4.9	1.7
ZW3	97.1	2.9	1.3	4.1	1.5
ZnO1	95.6	4.4	1.5	5.1	1.9
ZnO2	99.8	0.2	0.9	7.5	0.9

Table S2 - Results of analysis of Blue (BL) and Green (GL) emission decay kinetic fitted with a two or tree exponential decay model [17]. Here the single lifetime (τ) and the relative weight (A%) are reported. Values are given for all studied samples for the BL and GL emission integrated in the 420-440 nm and 490-510 nm region, respectively.

Blue Luminescence							
	A1 (%)	A2 (%)	A3 (%)	$\tau 1$ [μs]	$\tau 2$ [μs]	$\tau 3$ [μs]	$\bar{\tau}$ [μs]
ZW1	26.9	32.9	40.2	16.5	2.6	0.5	5.5
ZW2	22.6	28.4	49.0	17.8	2.4	0.5	4.9
ZW3	-	-	-	-	-	-	-
ZnO1	26.3	32.0	41.7	17.5	2.9	0.6	5.8
ZnO2	-	-	-	-	-	-	-
Green Luminescence							
	A1 (%)	A2 (%)	A3 (%)	$\tau 1$ [μs]	$\tau 2$ [μs]	$\tau 3$ [μs]	$\bar{\tau}$ [μs]
ZW1	33.9	38.8	27.3	15.1	3.1	0.7	6.5
ZW2	56.2	43.8	-	11.0	1.0	-	6.6
ZW3	25.0	75.0	-	16.3	1.7	-	5.3
ZnO1	38.6	40.8	20.6	15.9	3.6	0.8	7.8
ZnO2	18.4	47.5	34.1	18.2	4.2	0.8	5.6

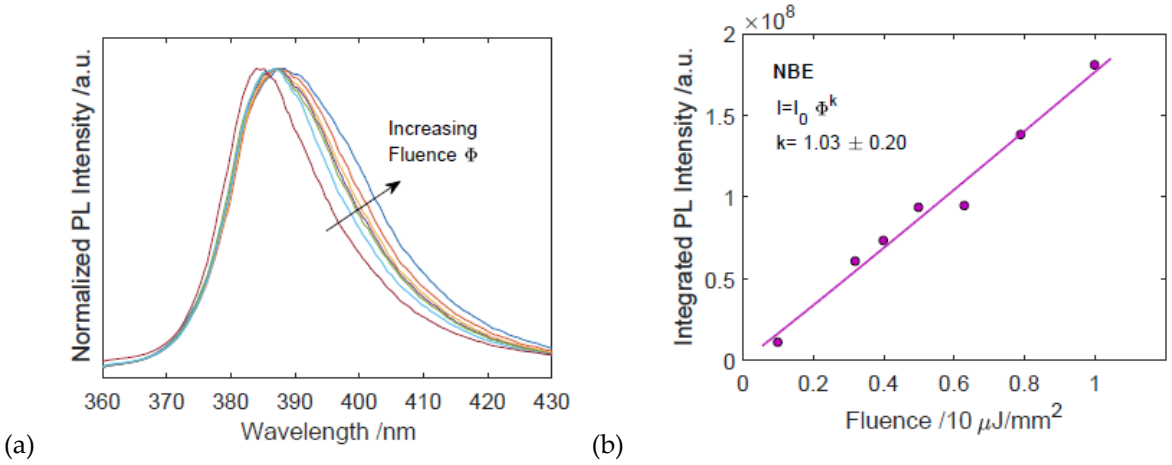
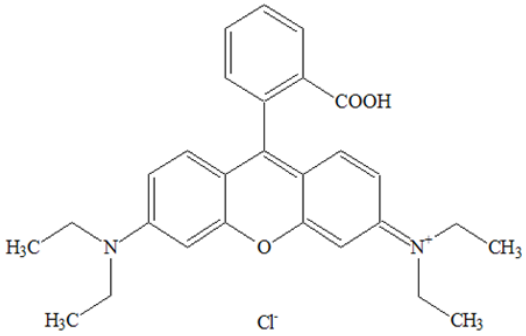


Figure S4 - **(a)** NBE emission at different excitation fluence. The left shoulder significantly increases in intensity with the increasing of the fluence value, causing a red-shift of the peak position. **(b)** Dependence of the NBE emission intensity on the fluence value. The integrated PL intensity is interpolated with a power function of fluence.

Photocatalytic Tests



Scheme S1 – Rhodamine B

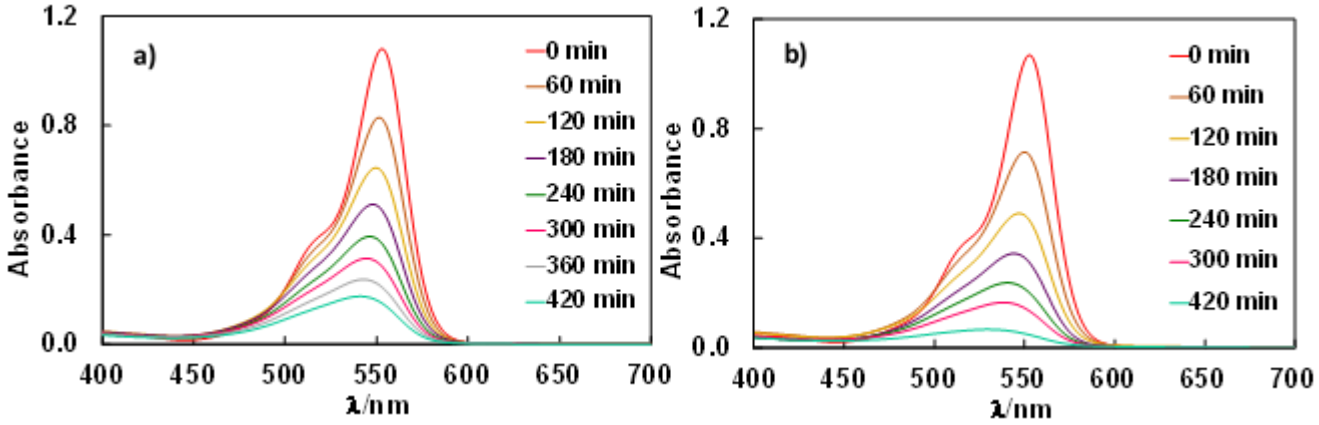


Figure S5 - Absorption spectra recorded during photocatalytic degradation of RhB under irradiation with a 420 nm cut off filter in the presence of a) ZnO1 and b) ZnO2 samples.