UV degradation of pigments: spectroscopic, morphological changes and mathematical expression.

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Objectives

The pigments used in objects of art and cultural heritage can change due to exposure to light, humidity, interventions, dirt, etc., which can change their color, consistency, resistance, etc. [1,2]. Thus, the precise characterization of the constituent materials of the pigments: inks, binders (mediums), impurities, allow us to understand their properties and the changes that occur over time. Our goal is to systematically study pigment degradation processes by UV and we are particularly interested in this work in the study of Cochineal Carmine and Titanium White(TiO_2). For this study we used Atomic Force Microscopy (AFM) in Tapping and QNM[3]
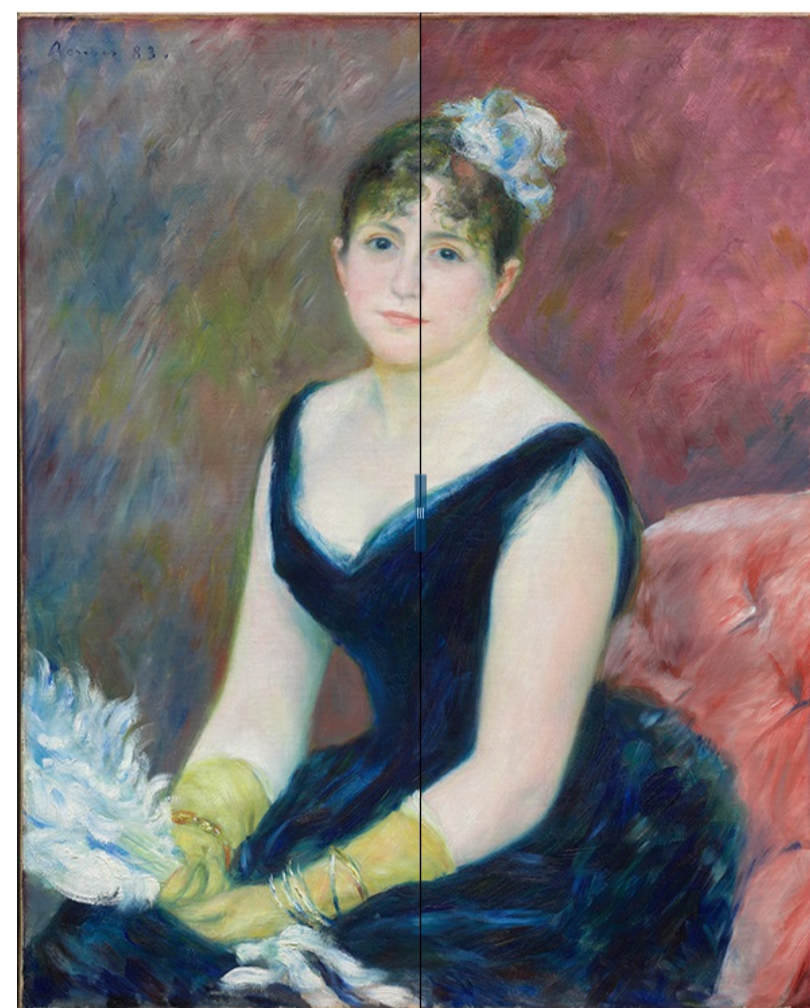

Figure 1: "Madame Léon" - Pierre August Renoir 1883. current coloring left, right. digitally retrieved "original" coloring. An example of degradation

Methods and Procedures

We used Atomic Force Microscopy in two modes: Tapping and QNM. In Tapping Mode, as the sweep occurs, the interaction forces between tip and sample vary the amplitude of oscillation, almost always decreasing it. Therefore, to provide an analysis, it is necessary that the amplitude of oscillation is kept constant, implying a constant average tip/sample distance. In QNM Mode, using the AFM Tapping scanning mode, the Quantitative Nanomechanical Microscope (QNM) is able to extract, at the same time, information about several physical and mechanical properties, such as elastic modulus, adhesion, water dissipation, energy and the maximum deformation of the sample, in addition to its topography.

What differentiates the two modes is the resonance frequency, while in Tapping we have 100 to 400 KHz , in QNM we have 1 to 2 KHz. In figure 2a, we have the scheme (TCT - Carmine Titanium Screen) screen, carmine over the entire surface, and only half with TiO_2 + Oil. After drying, the two parts were measured in Tapping Mode, after approx. 18 days in the degradation chamber, the sample received approximately 0.8 MegaJ of UV radiation, here it was chosen to take the measurement in QNM mode because the roughness of the sample caused interference in the measurement.
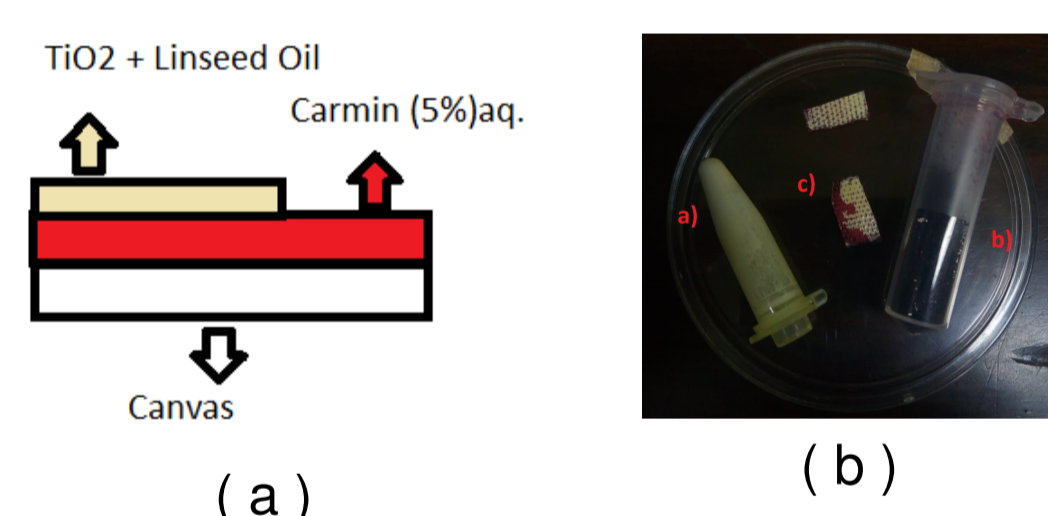

Figure 2: a) Diagram of canvas, carmine, titanium, b) b.a) Titanium + Linseed Oil, b.b) Dry Cochineal Carmine, b.c) TCC sample

Equipment and Analysis

A Scanning Probe Microscope NanoScope IIIA** manufactured by Bruker was used, with accessories to perform AFM Tapping and QNM mode.
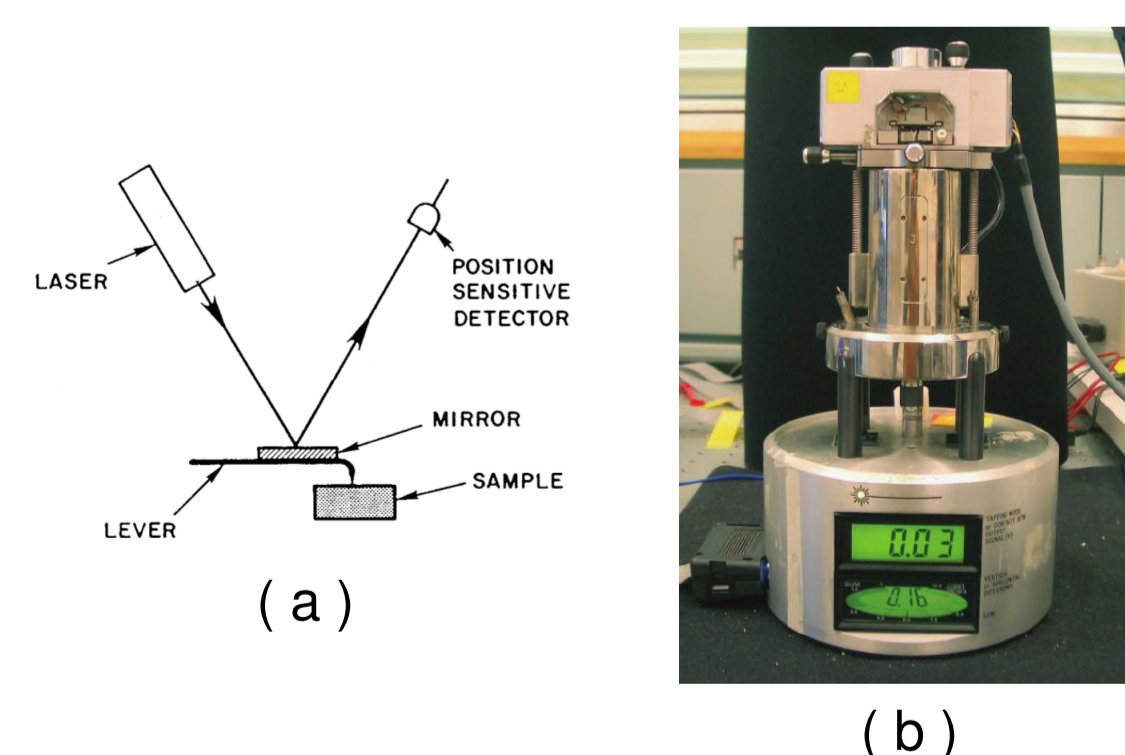

Figure 3: a) Demonstration of how the analysis of the movement of the probe in an AFM takes place from the reflection of the laser on the free end of the cantilever,b)NanoScope IIIA (Bruker)
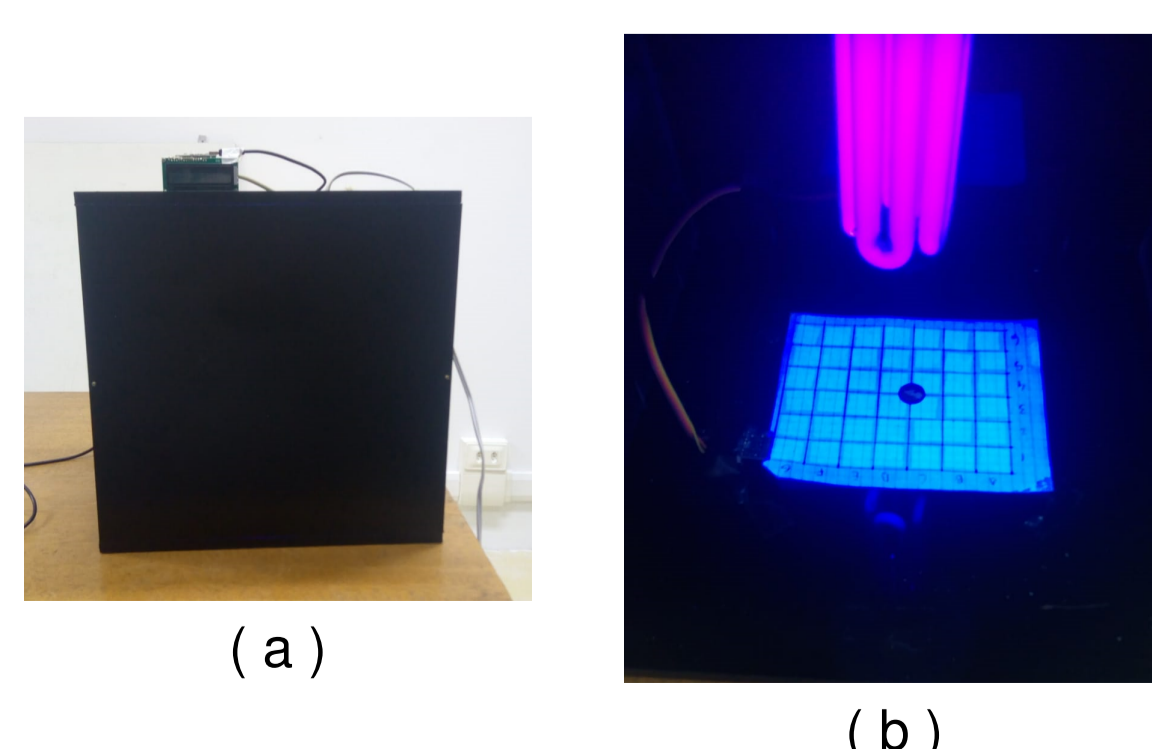

Figure 4: a) UV Degradation Chamber, b) Inside the degradation chamber already with sample

Experimental Results

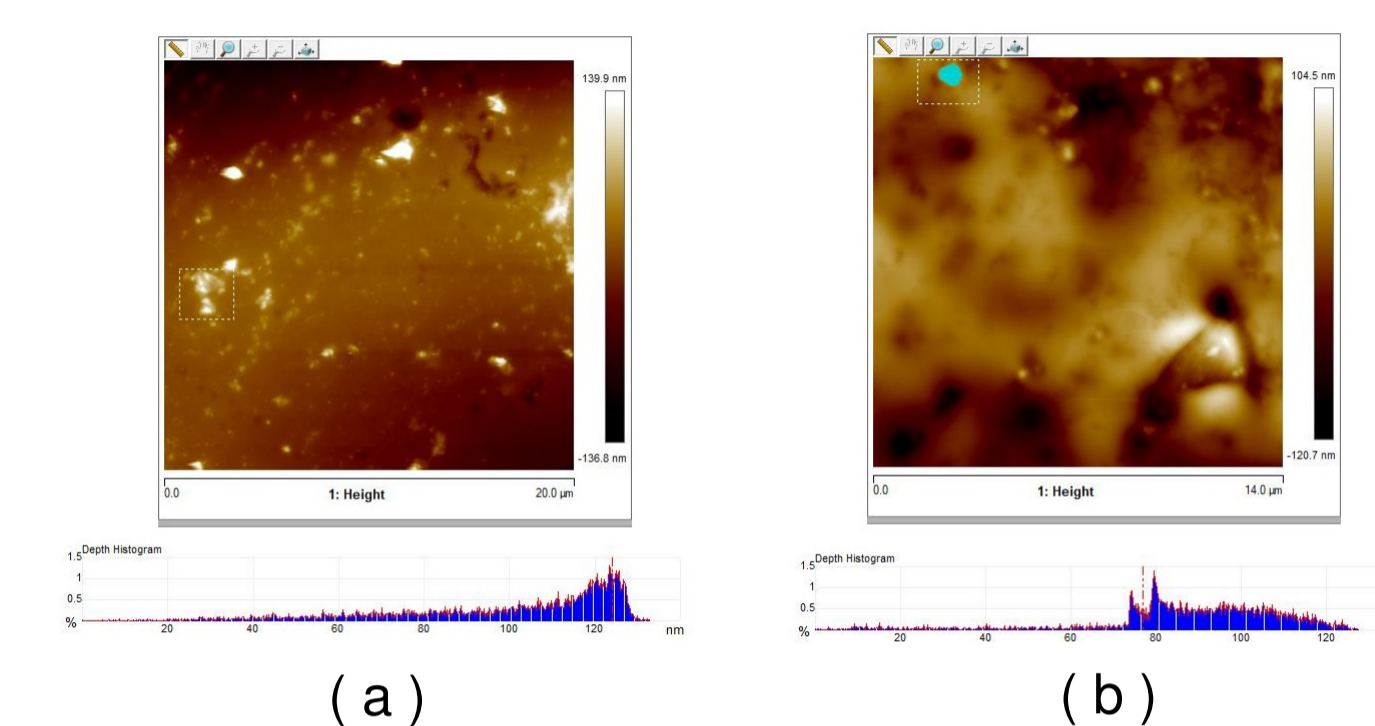Figure 5: Cantilever and its rounded tip. Tip radius approx. 10nm

Figure 6: a) TiO_2 Crystal Before UV Degradation, with height in the order of 124 nm, b) TiO_2 Crystal after UV Degradation, with height in the order of 77 nm
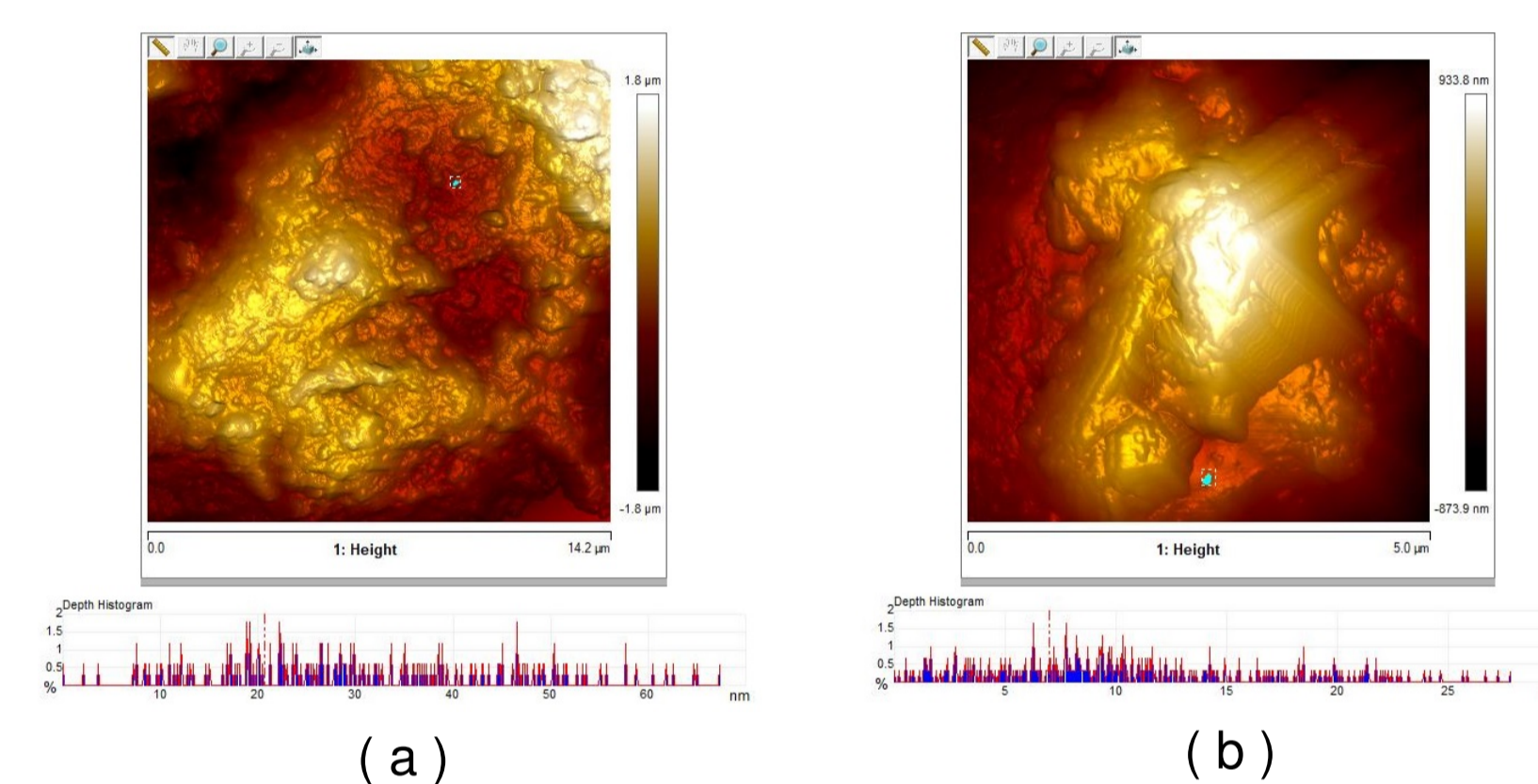

Figure 7: a) Carmine Before UV Degradation, with a height of around 20 nm, b) Carmine after UV Degradation, with a height of around 6 nm

Conclusions

We see that after degradation, the average height of the Titanium crystal and the Carmine agglomerate decreased in the order of 1/2 and the surface became less rough, even revealing the fibers of the screen. Something to note in carmine was the formation of possible spherical agglomerates.

This can show us, without damaging small samples, the potential of imaging by atomic force microscopy and how the morphology changes in the process.

Clearly other investigations are needed such as SEM, SERS-Raman, etc.
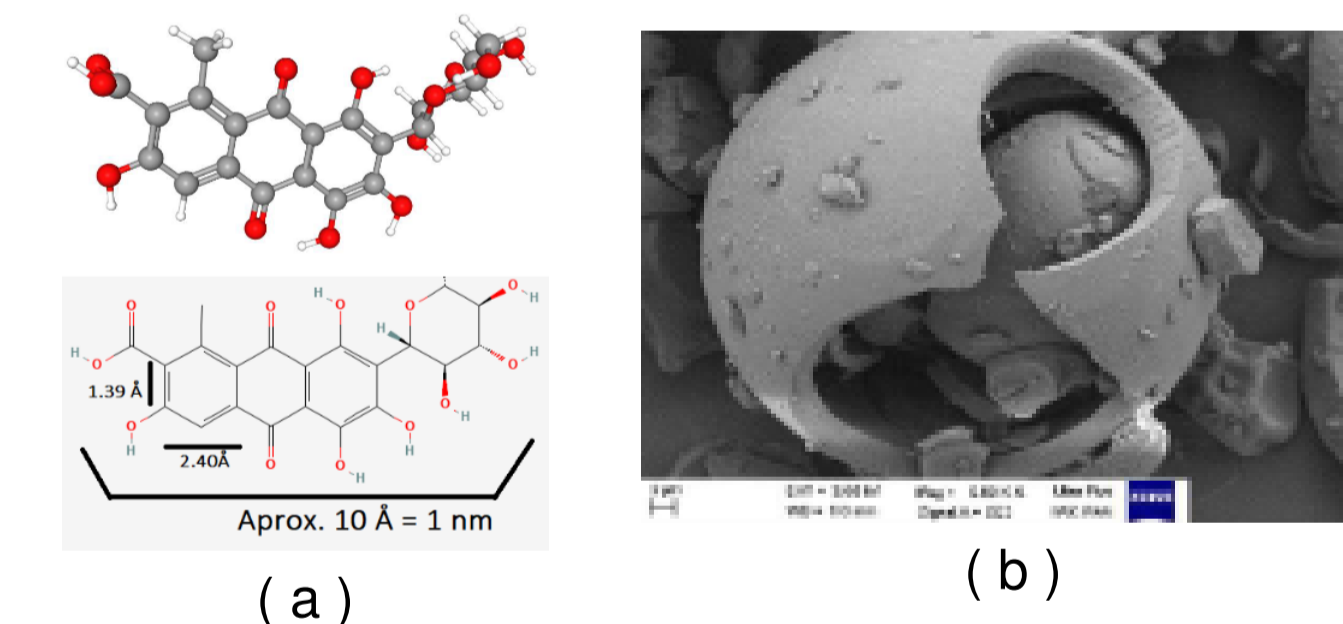

Figure 8: a) theoretical size of the carminic acid molecule, b) morphology by SEM[4] carminic acid cluster

Another investigation being studied is a mathematical modeling of damage in the color of pigments, such expression[5] is given by:

$$D_n = \int_{\lambda_1}^{\lambda_2} S(\lambda) f_n(\lambda, Q) \, d\lambda$$

Where D is the damage , S is the spectral distribution of absorption and reflection and f_n the exposure function (Watts.hour / m^2). Such parameters can be obtained via the FORS technique.
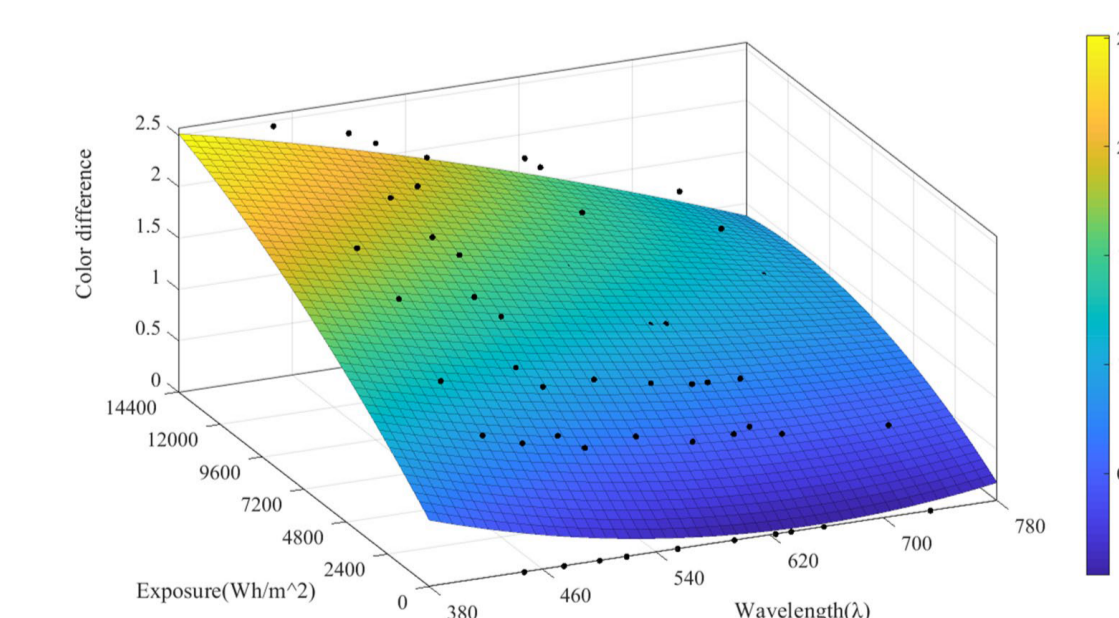

Figure 9: The three-dimensional variation surface of graphite color difference varying with SPD and exposure

Bibliographic References

1) Cannon J, Cannon M (2002). Dye Plants and Dyeing (2 ed.). A C Black. pp. 76–80. ISBN 978-0-7136-6374-7.

2) Milane C., Monico L., Melo M. J., Fantacci S.,Angelin E.M., RomaniA., Janssens K. (2018). Photochemistry of ArtistsQ Dyes and Pigments: Towards Better Understanding and Prevention of Colour Change in Works of Art. Angew, Chem. Int. Ed. 2018, 57, 7324 – 7334.

3) Global mapping of live cell mechanical features using PeakForce QNM AFM - January 2020 - Biophysics Reports 6(1)- DOI: 10.1007/s41048-019-00103-9

4) Marzec, Anna, Bolestaw Szadkowski, Jacek Rogowski, VYaldemar Maniukiewicz, Dariusz Moszynski,Przemystaw Rybinski, and Marian Zaborski. 2019. "Carminic Acid Stabilized with Aluminum-Magnesium Hydroxycarbonate as New Colorant Reducing Flammability of Polymer Composites" Molecules 24, no. 3:560. https://doi.org/10.3390/molecules24030560

5)The mathematical expression of damage law of museum lighting on dyed artworks- Rui Dang*, Baoping Wang, Xiangyang Song, Fenghui Zhang Gang Liu - Scientific Reports — (2021) 11:10951 — https://doi.org/10.1038/s41598-021-90520-z

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