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Characterization of dye isomers in a purple/red Mayan hybrid nanocomposite using Surface-Enhanced Raman Spectroscopy (SERS)

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***Abstract* – An extremely stable hybrid nanocomposite is obtained by grinding and heating microporous palygoskite clay with the methyl red dye. Such a complex shows the very same physical/chemical properties of the renowned *Maya Blue* – an ancient pigment produced by Mayas in Pre-Columbian America – remaining substantially unaltered when attacked by strong acids, alkali or solvents. Incorporation in the host tunnels stabilizes the methyl red molecules, preventing both deterioration and color changes. The molecular features of the encapsulated dye molecules were studied by means of Surface-Enhanced Raman Spectroscopy (SERS), a useful technique to analyze adsorbates even at very low concentrations. In palygorskite pores, methyl red exists both in its neutral (azo) and in protonated (hydrazo) forms. Diffusion in the clay tunnels causes moderate ring deformations and distortions in the guest molecule, as reflected by the shift of selected Raman modes. Presence of several dye species in the host framework, each contributing to the nanocomposite colour, qualifies the studied complex as a polyfunctional organic/inorganic hybrid composite, fit for use in the Cultural Heritage and Materials Science fields.**

I. INTRODUCTION

Ancient Mayas in Pre-Columbian America produced *Maya Blue*, a famous blue pigment well known for its exceptional stability and resistance to chemical agents, by grinding and heating palygorskite – a microporous clay mineral – with the indigo dye. Such a composite material, when rediscovered in the XIX Century, immediately attracted the interest of the Scientific Community, as contrary to other pigments it showed an outstanding stability. Maya Blue can resist the attack of strong acids, alkali and/or solvents, leaving both its colour and crystal structure unaltered [1].

Basing on these evidences, the extraordinary sorption properties of palygorskite were probed to produce a new class of nanostructured materials, exploiting the feasible fixation of different dye molecules in the host matrix, aimed to create a palette of environmental-friendly pigments granted by limited toxicity and low production expenses. Promising results were achieved by incorporation of methyl red in palygorskite. Similarly to the synthesis of *Maya Blue*, methyl red diffusion in the tunnels that permeate this clay mineral crystal structure can be obtained by grinding proper amounts of the dye with the host and moderately heating. This procedure allows dye diffusion within the clay pores and stabilization through formation of specific host/guest interactions. The resulting hybrid composite shows the same stability of its renowned blue analogue, maintaining its purple/reddish hue and preventing colour changes in spite of severe physical/chemical attacks – such as drastic pH fluctuations or prolonged solar/UV-A irradiation [2-4].

II. MATERIALS AND METHODS

Crushed, purified palygorskite (from Mexico) was mixed and hand-ground with 2 wt % of methyl red powder (from Carlo Erba), adding few drops of ethanol. Such an orange mixture was dispersed in a Petri dish with diluted HCl (20%) and heated up to 140°C for 20 hours. The resulting red-purplish compound was Soxhlet-extracted in ethanol to remove the dye-surplus, turning to a bright purple-violet hue.

Silver colloidal pastes were prepared according to the procedure reported in Idone et al. [5]. Conventional Raman and SER measurements were performed with a Renishaw (Stonehouse, United Kingdom) In-Via micro-Raman spectrometer. SER signals were obtained by focusing three different laser beams (532, 633 and 785 nm) onto the sample through a 50X or 100X magnification objective of a Leica (Wetzlar, Germany) DM2500 M optical microscope, coupled to the spectrometer.

III. RESULTS AND DISCUSSION

The conventional Raman approach, often applied to the study and characterization of nanocomposites, is sometimes limited by the low amounts of guest molecules adsorbed by the host, as well as by the strong fluorescence effects eventually induced by inorganic substrata. This is the case of the investigated hybrid nanocomposite. Surface-Enhanced Raman Spectroscopy (SERS), on the other hand, represents a viable tool to overcome such problems, as it can exalt the intensity of the scattered Raman signals and improve the method sensibility. SERS – performed with silver colloidal pastes - helped in further investigating the details of methyl red incorporation in the tunnels of palygorskite, especially for what concerns the subtle identification of the peculiar dye species interacting with the host framework, as well as to inspect their mutual host/guest interactions.

Comparison of SER spectra of pristine methyl red with those collected on the related palygorskite-complexed hybrid composite, proved that vibrational modes ascribable to both the azo (neutral) and hydrazo (protonated) species of the dye are unambiguously present throughout all the patterns. Both forms of the dye, therefore, coexist in the hybrid composite as well as in the pure dye. In particular, the SER spectrum of the composite is clearly dominated by bands related to the protonated form, whereas those modes clearly associated to the neutral one are evidently subordinated. Apparently, encapsulation of methyl red in the host might favour progressive transformation of the neutral to the protonated dye species. However, the troublesome evaluation of band intensities in SER spectra causes such an interpretation to be uncertain. Besides, partial protonation of the dye after interaction with the Ag colloidal paste cannot be excluded.

Detection of slight to modest band shifts between the SER spectra of pristine methyl red and that of the related palygorskite-based composite, suggest that the encapsulated dye may undergo specific ring deformations and/or distortions after incorporation in the clay framework and formation of host/guest interactions

IV. CONCLUSIONS

The unambiguous existence, in the host clay tunnels, of different topological methyl red isomers – namely neutral and protonated species – causes the studied material to be suitably considered as a polyfunctional organic/inorganic hybrid composite – a fitting definition also for the famed blue-analogue formed by indigo fixation in palygorskite (Maya Blue) [6].

These different dye species are bound to the hosting matrix by means of specific host/guest interactions – which account for this material exceptional stability, each contributing to the composite specific colour.

These peculiar physico-chemical properties cause the studied nanocomposite to be a valid, ecological surrogate to other synthetic pigments, used nowadays in the Materials Science and Cultural Heritage fields.

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