

Confocal Raman Microscopy: a powerful technique to characterize intercalated materials

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Abstract – Films of vanadium pentoxide xerogel composites VXG-MTRPyP (MTRPyP = *meso*-tetraruthenated metallopyridylporphyrins) were studied by confocal Raman microscopy. All composites exhibited spectral homogeneity at the optical resolution limit. A strong band at 880 cm⁻¹ was observed for the intercalated metallo-tetraruthenated species, in contrast to the simply metalated or just ruthenated species. These results revealed a special mode of interaction between the *meso*-tetraruthenated metallopyridylporphyrins and lamellar V₂O₅, which is not detectable by X-Ray diffraction.

Confocal Raman microscopy is a powerful tool to investigate the chemical micro-homogeneity of nanocomposites, particularly to acquire vibrational information about the chemical environment inside the matrix. Its application to the characterization of a novel class of nanocomposites comprising porphyrin/(Vanadium pentoxide xerogel) is reported in this work. The porphyrins and their respective composites were previously synthesized and characterized, including their electronic and spectroscopic properties. This type of material has proved highly sensitive for gas detection in amperometric sensors [1,2,3]. The confocal Raman spectra of such vanadium pentoxide xerogels (VXG) incorporating *meso*(3- and 4-pyridyl)metalloporphyrin (Metal M = Cobalt, Nickel, Iron, Manganese) species coordinated to four [Ru(bipy)₂Cl]⁺ complexes (Figure 1) were examined at 532 nm excitation wavelength (Nd:YAG laser). When these supermolecules were incorporated into VXG, the resulting composites exhibited characteristic electronic broad bands in the 450 – 800 nm range. For obtaining the Raman spectra at resonance condition, the scans were recorded using 133 nm/pixel resolution (Nikon N.A.=1,25). Spectral homogeneity and intensity-topography relationship were obtained for all scans (Figure 2. *Left*). The tetraruthenated porphyrins exhibited characteristic bands of the VXG and porphyrin species, however a distinct broad and strong Raman band was observed at 890 cm⁻¹ (Figure 2. *Right*). This signal coincides with the vibrational peak $\nu(\text{O-V}_2)$ of lamellar V₂O₅ but is only observed in the presence of the tetraruthenated metalloporphyrin species, suggesting a special mode of interaction between the metalloporphyrin center and the vanadium(V)-O lattice, involving the formation of M(III)-O-V(V) bonds, inside the cavities of the supramolecular tetraruthenated species. (Acknowledgements: CNPq process: 142519/2008-1, and FAPESP).

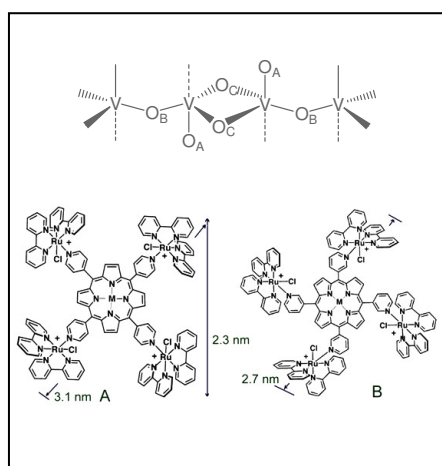


Figure 1: Structures for V₂O₅ and M-TPyP

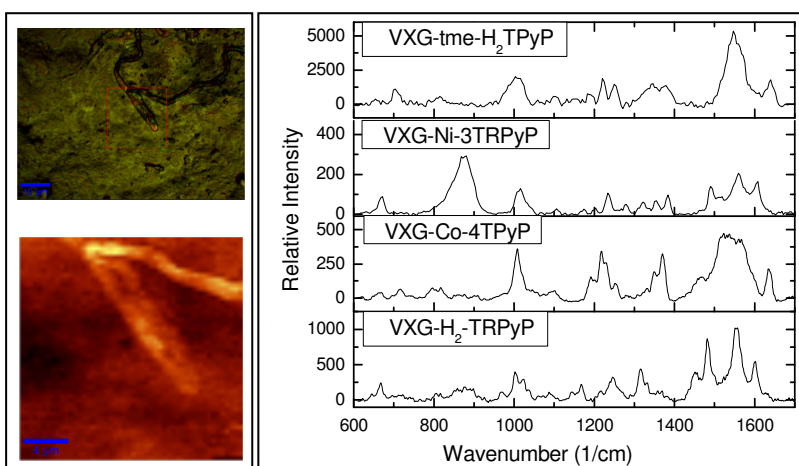


Figure 2. *Left*: Optical image and Raman 1490 cm⁻¹ (bipy) band imaging. *Right*: Raman spectra of the composites.

References

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