

Mapping different vibrational modes of CM- β CD probe on polymorph of TiO₂ by Confocal Raman Microscopy

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Abstract – The presence of anatase rich and rutile rich domains on nanocrystalline films of P25 TiO₂, as well as the distinct coordination modes of carboxylates on those phases, were revealed by confocal Raman microscopy, a technique that showed to be suitable for imaging the chemical morphology down to submicrometer scale.

The advancement of nanoscience and nanotechnology is leading to the development of increasingly intricate systems, exhibiting very often unpredictable combinations of two or more materials or phases^[1]. This is particularly critical in the cases where inorganic/organic hybrid interfaces are involved, turning into a real challenge the evaluation and understanding of their detailed chemical composition and distribution. In this regard, techniques such as SEM, EDS and TEM which are nicely suited for inorganic solids, become rather limited when molecular materials and interfaces are considered. Thus, in this work we report the successful use of confocal Raman microscopy for direct imaging the chemical morphology of mesoporous titanium dioxide interface, clearly evidencing the segregation of rutile and anatase nanoparticles as well as the distinct coordination mode of adsorbed carboxylate species.

The better comprehension of such a mesoporous interface is necessary for the development of more efficient dye sensitized solar cells and photocatalysts. In this sense, an imaging technique capable of showing the actual distribution of rutile and anatase phases, as well as of the adsorbed molecular species, would be greatly important.

Mesoporous films of TiO₂ (4-8 μ m thick) were prepared dispersing a colloidal emulsion^[2] on cover slip (A = 1 cm², was delimited with Scotch tape), allowing them to dry at room temperature and firing at 450 °C for 30 min. Confocal Raman Microscopy images were obtained in a WITec Alpha 300R microscope, quipped with a 532 nm solid state laser and 100X objective (N.A. = 0.8). The SEM images were obtained in a Jeol JSM-7401F field emission scanning electron microscope.

The mesoporous film of P25 titanium dioxide appears as a network of interconnected 20-60 nm grains, in the scanning electron microscopy image (Fig.1). Contrasting Raman images of mesoporous TiO₂ films (Fig. 2) have been obtained by plotting the intensity of typical rutile, e. g. 448 cm⁻¹ (right), and anatase, e. g., 398 cm⁻¹ (left), peaks as a function of the xy position, thus revealing their actual distribution in the film. Confocal Raman images showing the CM- β CD distribution on a rutile/anatase nanocrystalline film obtained simultaneously monitoring the $\nu_{as}(\text{COO})$ bands at 1652 and 1605 cm⁻¹, as well as $\nu(\text{C-H})$ peak at 2951 cm⁻¹ (Fig. 3). The chemical morphology of such interface was successfully probed by confocal Raman microscopy, a technique which was proven powerful, sensitive and flexible enough for imaging not only the rutile and anatase submicrometer sized domains, but also the distinct coordination modes of anchored carboxylate species.

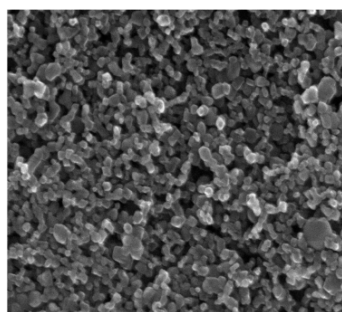


Fig. 1- Scanning electron microscopy images showing the morphology of mesoporous P25 film fired at 450 °C, for 30 min.

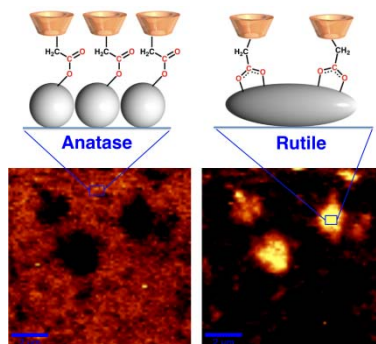


Fig. 2- Confocal Raman Images showing the morphology of rutile /anatase distribution on a nanocrystalline. 448 cm⁻¹ (right) and 398 cm⁻¹ (left).

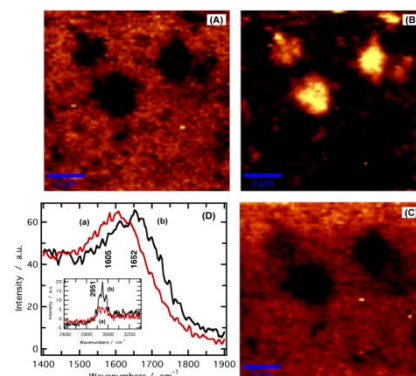


Fig. 3- Band at 1652 (A) and 1605 cm⁻¹ (B); as well as the $\nu(\text{C-H})$ peak at 2951 cm⁻¹ (C). The Raman spectra at (a) rutile rich and (b) anatase rich domains are shown in (D).

References

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