

Sensitization of TiO₂ by a New Polypyridine Dye Role of the Electron Donor

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A new dye, a Ru(II) complex containing only terpy ligands (TPP) was synthesized and grafted on nanocrystalline TiO₂ anatase thin film electrodes; its chemical structure is given in figure 1.

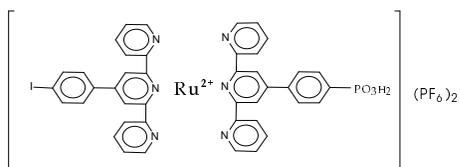


Figure 1 Chemical structure of TPP complex

The topic of this study is to characterize by Raman spectroscopy the role played by the electron donor in solution with respect to the complex adsorption on TiO₂.

Experimental

TiO₂ substrates were prepared by a sintering technique using Degussa P25 powder [1].

The characterization by *in situ* Raman spectroscopy was performed in presence of two different electron donors, 0.1 M KI and 0.1 M hydroquinone (HQ), in 10⁻³ M HClO₄ aqueous solutions.

Results

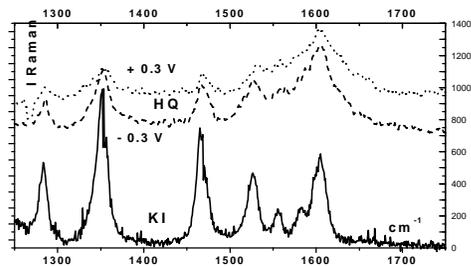


Figure 2 Raman spectra ($\lambda = 514.5$ nm) of TPP adsorbed on TiO₂ polarized at 0.3 V (KI) and -0.3 V (HQ) or 0.3 V (HQ)

The spectra obtained in figure 2 with green laser excitation are typical of the adsorbed terpy ligand in the rings stretchings spectral range. Features related to phenylphosphonic group do not appear. The band at 1580 cm⁻¹ is not present in the TPP powder; it appears *ex situ* as a shoulder and becomes an individualized vibration in the solution. The strong band at 1351 cm⁻¹ cannot be assigned to a known vibration in the different components of the complex. The band at 1530 cm⁻¹ disappears with red laser excitation which means that it is drastically

related to the Raman resonance. These bands can be considered as markers of the adsorption.

Noticeable differences appear between the two electron donors. The bands are broader in presence of HQ; furthermore, the spectra are independent on the voltage in presence of KI, while in presence of HQ an 1604 cm⁻¹ band is enhanced when the voltage becomes more anodic. This band could be assigned to HQ and a competitive adsorption of this molecule on TiO₂, however a strong band at about 1250 cm⁻¹ would be expected in the same time, which is not the case. The presence of HQ on the sample cannot be therefore detected.

On the contrary, the low frequency spectral range, i.e. the region of the anatase Eg vibration peak (143 cm⁻¹) allows to focus on the iodine, (triiodide anion) absorption. The Eg peak is interesting by itself, because its wavenumber as well as its FWHM are directly related to the anatase nanocrystallinity [3] Strong differences are observed in presence of KI with the presence of two new peaks centered respectively at 112 and 170 cm⁻¹, as shown in figure 3 obtained under open circuit potential conditions. These peaks are not observed with HQ.

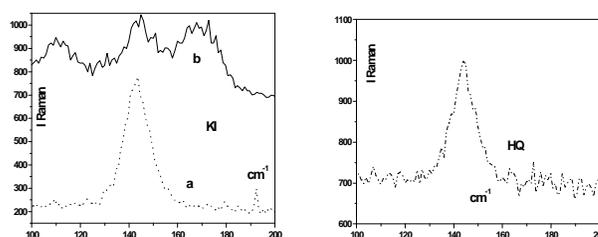


Figure 3 TPP complex low frequency spectra obtained in presence of KI a: *ex situ* b: *in situ* in open circuit; in presence of HQ, *in situ* in open circuit.

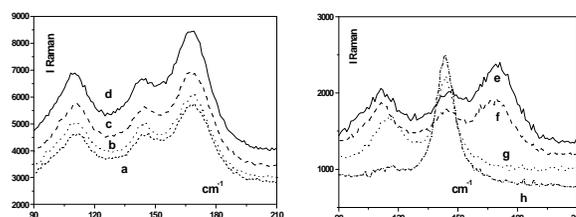


Figure 4 Raman spectra of TPP adsorbed on TiO₂ polarized in presence of KI at a: 0.3 V; b: 0.2 V; c: 0.1 V; d: 0 V; e: -0.1 V; f: -0.3 V; g: -0.7 V; h: -0.9 V

As shown in figure 4, their intensity seems to be independent on the anodic potential but strongly depends on the cathodic potential. They completely disappear between -0.7 and -0.9 V/SCE. Their appearance is directly related to the presence of the iodide ions in the electrolyte. The iodide ions are therefore able to be adsorbed as I₃⁻ on the TiO₂ sample, and to block certain sites which cannot be occupied by the dye phosphonate group.

References

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- [3] P. Falaras, A. Hugot – Le Goff, M.C. Bernard, A. Xagas, *Sol. Energy Mat., Sol. Cells*, 64. (2000), 167