Sensitization of TiO_2 by a New Polypyridine Dye. Characterization by UV-Vis, FTIR, Raman and EI Spectroscopies

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Interesting values of photocurrents were obtained using different Ru(II)-polypyridyl (bipy or terpy) complexes grafted on high roughness/porosity TiO_2 anatase thin film electrodes. It is therefore a challenge to find the "best" antenna molecule allowing to obtained a high photoconversion yield.

Here, a new complex (TPP) is studied that presents the theoretical interest to contain only terpy ligands; its chemical structure is given in figure 1.

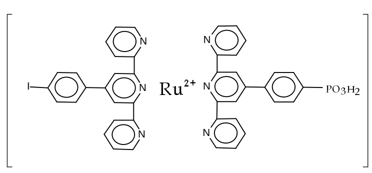

Figure 1 Chemical structure of TPP complex

The topic of this preliminary study is to characterize the molecule and particularly its adsorption on TiO_2. Its properties are therefore compared with those of another dye, $RuL_2(NCS)_2$, i.e. Ru 535 (Solaronix).

Experimental

Nanocrystalline TiO_2 was prepared by a sintering technique [1] from a colloid suspension (0.5 g Degussa TiO_2 powder 0.11 ml acetyl acetone, 2.8 ml water, 1 drop of triton X-100) on conducting glass, dried at 100°C during 15 min (solvent evaporation) then at 450°C during 30 min (cohesion between particles). Pure anatase gel (Ti-Nanoxide T from Solaronix) was also used.

Surface derivatization was achieved by immersing the TiO_2 thin film electrodes for one hour in a 10^{-4} ethanolic solution of the complex.

The optical response of the dye in ethanol (figure 2a) or adsorbed on TiO_2, (figure 2b) presents a MLCT absorption band with a maximum at 490 nm.

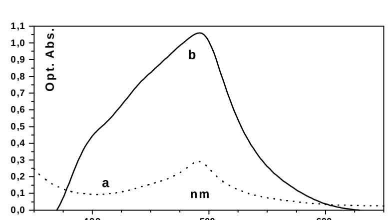

Figure 2 Optical Absorption .of TPP;
a: powder in ethanol; b: adsorbed on TiO_2

Thin layer photoelectrochemical cells were also studied, with the structure: SnO_2 /TiO_2 /TPP /electrolyte/ Pt/ SnO_2; the electrolyte is 0.1 M LiI + 0.01 M I_2 in propylene carbonate.

The characterization by EIS and *in situ* Raman spectroscopy (with a green exciting laser light) were done in 10^{-3} M perchloric acid + 0.1 M KI solution.

Results

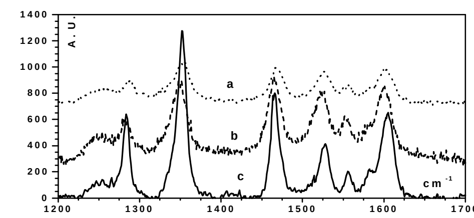

Figure 3 Raman spectra of TPP; a: powder;
b: cast on TiO_2; c: cast on TiO_2 and immersed in solution (open circuit); λ_{ex} = 514.5 nm

In figure 3, the spectrum of TPP as prepared (a) is compared using Raman spectroscopy to the spectra after grafting on titanium oxide, *ex situ* (b) and *in situ*, at open circuit (c). Spectrum a is not characteristic of the terpy ligand, but similar to the spectrum of adsorbed terpy ligand [1], which corroborates the ionic nature of the pristine dye. The phenyl ring present between the surface and the terpy group must have an influence on the terpy vibrations; however, features able to be related to phenylphosphonic group do not appear in the spectra. On the contrary, FTIR allows to identify the ν (P=O) vibration from the three bands at 1240, 1140 and 975 cm^{-1}. The second peak shifts from 1138 in the free complex to 1143 cm^{-1} for the TiO_2 chemisorbed complex.

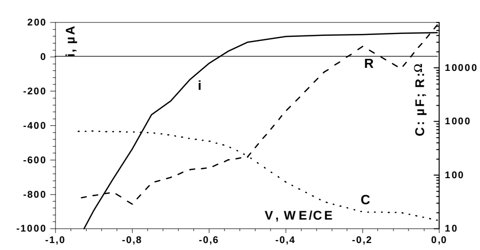

Figure 4 Current-voltage curve of a sandwich cell using Ru 535 dye, under an irradiance of 10 mW. cm^{-2}; variations of R and C

The cell EIS Nyquist diagrams are characterized by three capacitive loops. The loop centered around a few Hz corresponds to the TiO_2 /electrolyte interface; it is simply described by a (R, C) parallel circuit. At the voltage (≈ -0.5 V between the working electrode and the counter electrode) when the photo current appears, figure 4 obtained with a Ru 535 as a dye shows that R becomes very large (no more recombination) and C decreases strongly, showing most of injected electrons are extracted from TiO_2 grains.

References

[1] A. Xagas, E. Androulaki, A. Hiskia, P. Falaras, Thin Solid Films, 357, (1999), 173