“Sensitization of SnO_2 by Ru(II)-polypyridine complexes investigated by in-situ resonance Raman Spectroscopy”

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Large band-gap metal oxide semiconductors in the form of nanocrystalline thin film electrodes are mains used as the photoanode material in dye-sensitized solar cells. Recently, detailed investigations performed by Resonance Raman spectroscopy during the cell operation, revealed the presence of vibration bands attributed to new species that are formed at the dye/semiconductor (TiO_2) interface. In order to check the influence of the semiconductor substrate, in this study we present the corresponding results obtained with dye-sensitised SnO_2 thin films. This choice is justified by the fact that SnO_2, a material that has been widely used in many electrooptical devices, is one of the few stable wide band gap semiconductors (E_g=3.6 eV) with a conduction band potential more positive than that of TiO_2.

Experimental

Transparent, nanostructured SnO_2 thin films were prepared on conductive glass: As starting material, a 15 wt % SnO_2 colloidal dispersion in water with K^+ as counterion was used without dilution. Surface derivatization of the tin oxide was achieved by immersing the SnO_2 thin film electrodes overnight in a 10^{-4} dry ethanol solution of the Ru535 complex. The cell assembling was completed by introducing the electrolyte (Iodolyte TG 50) between the photoelectrode and a platinized SnO_2 counter electrode.

Results

The Raman spectra (λ = 632.8 nm) of the bare SnO_2 film together with the assigned vibrational modes presented in Fig. 1 (left), consists of 4 major bands that can be classified into two groups: the normal interior phonon modes and the interface or surface phonon modes.

In-situ investigation in the lower part of the Raman spectra (wavenumbers below 250 cm^{-1} Fig.1 right), where no dye or SnO_2 bands are expected, two new peaks centered respectively at 112 and 167 cm^{-1} appear (the 1st overtone of 112 cm^{-1} appears also at ≈ 227 cm^{-1}).

The lower wavenumber band (112 cm^{-1}) was unambiguously assigned to the ν_1 vibration of the I_3^- moiety formed on the photoelectrode, following an already discussed mechanism.

Figure 1 Raman spectra of a bare SnO_2 film (left) and sensitized by Ru535 (right): ex situ spectra (solid line), in-situ with no polarization (short dash), spectra of the cell polarized at +0.4 V (short dot).

The other band that appears at 167 cm^{-1} at positive potentials (Fig. 2), always during the simultaneous presence of the chemisorbed dye and the I^-/I_3^- redox couple in the electrolyte solution, corresponds to a vibration in a chemically stable pyridine-iodine intermediate species (“DI “species) present at the dye/electrolyte interface. This species is abundant when SnO_2 heavily functions as an anode and “disappears” even at + 0.3 V. The range of stability in potential of the “DI” species is obviously shorter than the I_3^- stability range. Note that the stability and reversibility of the new bands were checked by performing a series of Raman experiments with different potential steps in the - 0.6 V / + 0.6 V range.

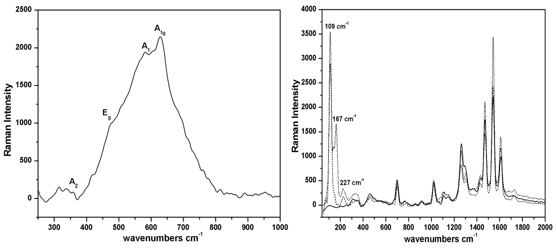
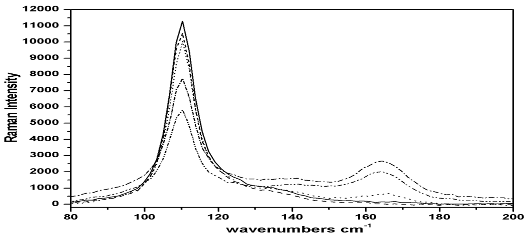


Fig. 2 Low frequency Raman spectra of Ru535/SnO_2 photoelectrochemical cell polarized at positive potentials: + 0.2 V (solid line), + 0.3 V (dash), + 0.4 V (dot), + 0.5 V (dash-dot) and + 0.6 V (dash-dot-dot).



References

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