Electrochemically deposited porous tin dioxide films for photoelectrochemical applications.

H. Cachet[a], T. Toupance[b] and V. Vivier[a]

a Laboratoire des Interfaces et Systèmes Electrochimiques, UPR 15-CNRS, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris CEDEX 05, France. E-mail : huc@ccr.jussieu.fr . Phone : 33 (0) 1 44 27 41 49 – Fax : 33 (0) 1 44 27 40 74.

b Laboratoire de Chimie Organique et Organométallique, UMR 5802 CNRS, Université de Bordeaux I, Cours de la Libération, 33405 Talence cedex, France.

Tin dioxide can be electrochemically synthesized via hydroxyde formation followed by decomposition into oxide and water. Hydroxylation is achieved by electrochemical reduction of dissolved oxygen or that of oxygen-containing species as, for instance, NO_3^-. With nitrate as OH^- source, concentrated solutions can be used allowing high deposition rates. Recently, SnO_2-based supercapacitors, with capacitance in the range 100-200 $F.g^{-1}$, have been fabricated by electrolysing $Sn(II)Cl_2$ / $NaNO_3$ / HNO_3 solutions potentiodynamically on stainless steel substrates [1]. From the point of view of solar energy conversion, such nanostructured films offer potentialities for dye sensitization and further utilization in photoelectrochemical cells.

In the present work in progress, a first step is devoted to study and optimize the conditions for the electrochemical synthesis of porous SnO_2 films from Sn(II) dichloride and acidic nitrate baths on F-doped SnO_2 substrates. The latter (about 300 nm thick) are deposited by spray pyrolysis on microscope glass slides at 500°C from $SnCl_4/NH_4F$/methanol solutions. The mechanism for electrochemical deposition can be assumed to be as follows. Hydroxyl ions are produced by reduction of nitrates according to the reaction:

$$NO_3^- + H_2O + 2e^- \Leftrightarrow NO_2^- + 2\ OH^-$$

We have also to consider the oxydation of tin from the II (Sn^{2+}) to IV (Sn^{4+}) oxidation state. Sn^{2+} can be oxidized into $Sn(OH)_3^+$ according to the reaction :

$$Sn(OH)_3^+ + 3\ H^+ + 2\ e^- \Leftrightarrow Sn^{2+} + 3\ H_2O$$

This step is followed by the formation of the tin(IV) hydroxide which decomposes into tin oxide and water :

$$Sn(OH)_3^+ + OH^- \Leftrightarrow Sn(OH)_4 \Leftrightarrow SnO_2 + 2\ H_2O$$

Fig.1 a and b show SEM images of a SnO_2 electrochemical deposit on top of a sprayed polycrystalline F-SnO_2 film. It was obtained by cycling potential between 0 and -1.1 V/SCE at 200 mV/s, the bath temperature being kept at 80°C. The thickness lies in the micrometer range. The deposit is highly dispersed with elementary quasi-spherical grains of about 100-200 nm in diameter. The as-deposited tin oxide layer is slightly yellowish. It becomes white after annealing in air at 380°C and well crystallized. Fig.2

shows the X-ray diffraction pattern after 1 hour annealing, which is characteristic of the cassiterite modification. By measuring the capacitive current when scanning the potential, the film capacitance was estimated close to 0.5 mF/cm^2 considering the geometric surface area.

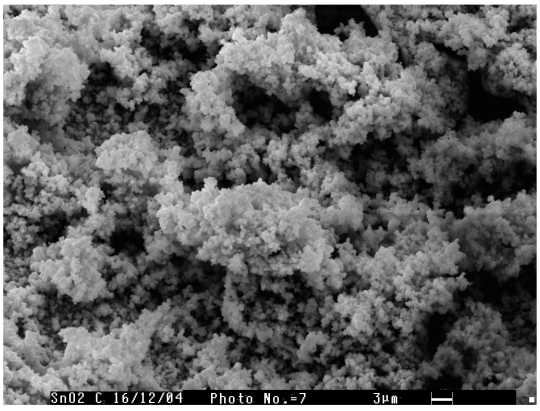

Fig.1a: *SEM image of potentiodynamically deposited SnO_2 from $SnCl_2$ in an acidic nitrate bath at 80°C. Magnification: 5000.*

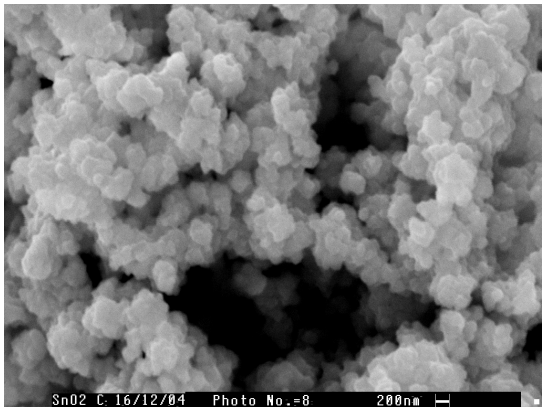

Fig.1b: *Same as in Fig.1a but magnification is 50000 showing elementary grains in the range 100-200 nm.*

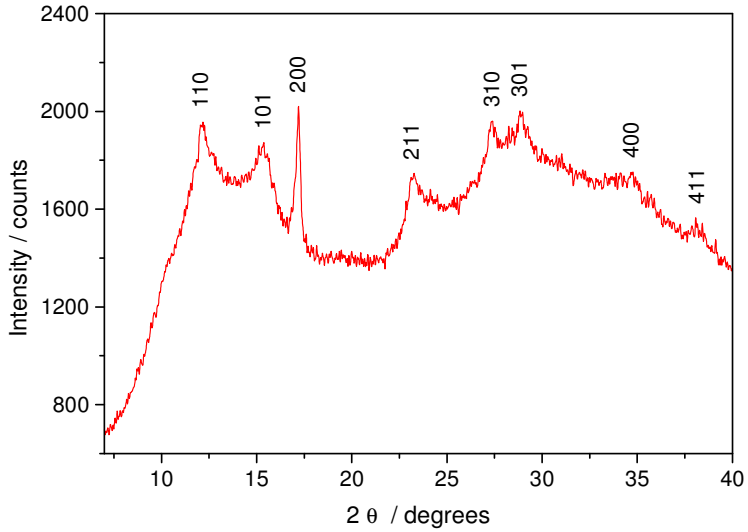

Fig.2 : *XRD diagram of electrochemically deposited SnO_2 after annealing at 380°C for 1 hour under air.*

The second step is concerned with dye sensitization. Two routes are explored: (i) usual dye chemisorption using commercially available dyes; (ii) efficient chemical grafting of new perylene-substituted trialkynyltins organic dyes *via* covalent Sn(oxide)-O-Sn-C(alkyl) bonds as demonstrated in the case of SnO_2 nanosized powders [2]. Photoelectrochemical tests will be hopefully presented at the Workshop.

References

[1] K. R. Prasad, N. Miura, *Electrochem. Comm.*, **6** (2004) 849.
[2] H. Cachet, V. Vivier, T. Toupance, *J. Electroanal. Chem.*, **572** (2004) 249.