

# Texture, Morphology and Photovoltaic Characteristics of Nanoporous F:SnO<sub>2</sub> Films

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**Abstract** – The nanoporous F:SnO<sub>2</sub> materials have been prepared through the controlled hydrolysis of fluoro(2-methylbutan-2-oxy)di(pentan-2,4-dionato)tin followed by thermal treatment at 400-550°C. The main IR features include resonances at 660, 620 and 540 cm<sup>-1</sup>. From the TG-DTG result, three main mass losses of 6.5, 13.3 and 3.8 at 81, 289 and 490°C are observed between 50 and 650°C yielding a final residue of 76.0%. The size of SnO<sub>2</sub> nanoparticles rose from 5 nm to 10-12 nm as the temperature of thermal treatment is increased from 400 to 550°C.

**Keywords:** F:SnO<sub>2</sub> film, Sol-gel, Nanoporous materials, Dye sensitized solar cells, Transparent conductive oxide

## 1. Introduction

Dye sensitization of nanoporous metal-oxide-semiconductors with a wide band gap provides a promising alternative method for fabrication of low-cost, high-efficiency photovoltaic systems, since a dye-sensitized TiO<sub>2</sub> cell was reported by Graetzel [1, 2]. In the related devices, various nanoporous oxide materials, for instance TiO<sub>2</sub> [1-3], SnO<sub>2</sub> [4, 5], Nb<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> [6, 7] or ZnO-SnO<sub>2</sub> [8, 9], have been usually utilized with adsorbed dyes such as transition metal polypyridine complexes [10, 11]. Compared to TiO<sub>2</sub>, SnO<sub>2</sub> offers several merits as oxide materials in such photovoltaic cells. SnO<sub>2</sub> is a better electron acceptor than TiO<sub>2</sub> owing to its more positive conduction band edge [4]. The conduction band potential of SnO<sub>2</sub> is approximately 0.4 V more positive than that of TiO<sub>2</sub> [9]. And SnO<sub>2</sub> has better long-term stability under UV-illumination due to its larger band gap [9]. It has been also reported that SnO<sub>2</sub> can be doped with fluorine or antimony in order to improve its electronic conductivity properties [12]. However, SnO<sub>2</sub>-based photovoltaic cells were found less efficient than the TiO<sub>2</sub>-based analogues [12]. The low efficiency is in part related to the intrinsic properties of SnO<sub>2</sub>. The photovoltage, for example, which is partly affected by the potential of the semiconductor bands, is expected to be lower in SnO<sub>2</sub>-based cells in comparison with TiO<sub>2</sub>-based cells [4, 5, 9]. The other

reason for efficiency losses may be connected to the structural properties of the nanoporous SnO<sub>2</sub> electrodes including, for example, the pore sizes, texture and morphology. Furthermore, no major effort has been made to enhance the photosensitization of SnO<sub>2</sub>, likely due to the lack of nanoporous F-doped tin dioxide materials (F:SnO<sub>2</sub>). In order to develop the use of SnO<sub>2</sub> in dye-sensitized solar cells, new approaches are therefore needed concerning highly conductive nanoporous SnO<sub>2</sub> materials and dye-oxide linkages. For SnO<sub>2</sub> fabrication several deposition methods exist, such as evaporation, sputtering, spray, chemical vapor deposition, and sol-gel method [13, 14]. In particular, the sol-gel method presents many advantages, and leads to very high-quality films. In this work, our aim is to develop new structural electrode materials used for photovoltaic cells that have the potential to yield nanoporous F:SnO<sub>2</sub> materials with uniform particle size by the sol-gel method. The nanoporous F:SnO<sub>2</sub> materials have been prepared through the controlled hydrolysis of fluoro(2-methylbutan-2-oxy)di(pentan-2,4-dionato)tin followed by thermal treatment. The discussion was focused on both thermal and morphology properties of the nanoporous F:SnO<sub>2</sub> materials obtained by tuning the temperature of the thermal treatment used to crystallize the materials.

## 2. Experimental

Fig. 1 shows the flow scheme for the sol-gel process employed for the synthesis of nanoporous F:SnO<sub>2</sub> materials. For the synthesis, SnCl<sub>4</sub>(99.995%) and HF 50%

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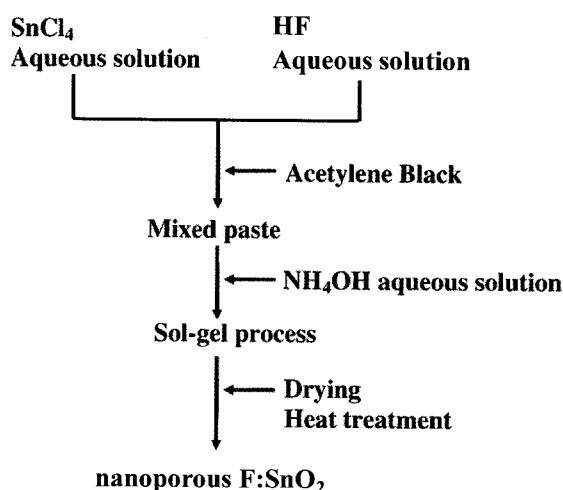


Fig. 1. Synthesis process of F:SnO<sub>2</sub> nanoporous material

in water (semiconductor grade) were purchased from Aldrich and used as starting materials. Acetylene black was purchased from Chevron Phillips Chemical Company. For the synthesis of nanoporous F:SnO<sub>2</sub> materials, 5.2 g of SnCl<sub>4</sub> and 0.38 g of HF 50% solution were dissolved in 20 ml of deionized water. Acetylene black of 0.4 g was added to this solution and then NH<sub>4</sub>OH aqueous solution was added drop by drop under constant stirring until it turned to a sol at ambient condition. This sol was heated at 120°C to transfer it into a dried gel. Being ignited in air at 650°C, an auto-combustion process took place and as-burnt powder was obtained. The sample was further calcined at 750°C for 30 min in air to get the nanoporous F:SnO<sub>2</sub> material. The chemical composition of the synthesized F:SnO<sub>2</sub> material was determined by inductively coupled plasma (ICP; Perkin Elmer, Optima 4300 DV) and ion chromatography (IC; Dionex, ICS-1500). Particle morphology and size were investigated by a field emission scanning electron microscope (FE-SEM; Hitachi, S-4300). Thermal analysis was carried out using a simultaneous thermal analyzer (STA; Scinco, STA S-1500) with a heating rate of 5°C/min.

### 3. Results and discussion

The IR spectra of the samples as-prepared and after calcination at various temperatures are given in Fig. 2. The gel was obtained 20 min after the end of the addition of water which gave a yellowish powder after aging for two days at room temperature and drying under vacuum at 80°C. The xerogel was then annealed at a temperature higher than 400°C for 30 min. In the following, the samples are labelled ST where T stands for the

temperature of the thermal treatment. The samples exhibited the intense and broad resonance owing to OH stretching modes ranging from ~3600 to ~2500 cm<sup>-1</sup> with a maximum at ~3428 cm<sup>-1</sup>. Below 2000 cm<sup>-1</sup>, the IR spectrum consists of a resonance at ~1627 cm<sup>-1</sup> due to water deformation mode, of bands characteristic of acetylacetonato ligands coordinated to tin at ~1568 and ~1537 cm<sup>-1</sup> (C-O) + (C-C), ~1425 and ~1351 cm<sup>-1</sup> (CH<sub>3</sub>), ~1027 and ~943 cm<sup>-1</sup> (CH<sub>3</sub>), and of wide bands at ~647 and ~560 cm<sup>-1</sup> assigned to Sn-O-Sn and Sn-O (belonging to Sn-OH groups) stretching vibrations, respectively[15]. After calcination, the main IR features include resonances at 660, 620 and 540 cm<sup>-1</sup> which fall in the range of the Sn-O stretching mode region and reveal the complete elimination of the chelating ligands. Slight variations in the relative intensities of these bands when the annealing temperature was increased up to 550°C disclose the changes in the shape and size of the SnO<sub>2</sub> particles owing to the sintering process [16].

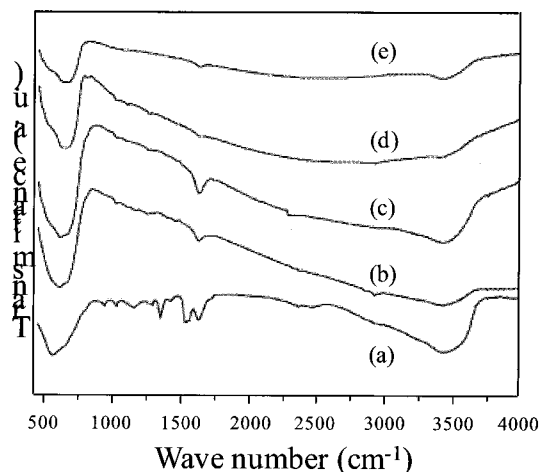
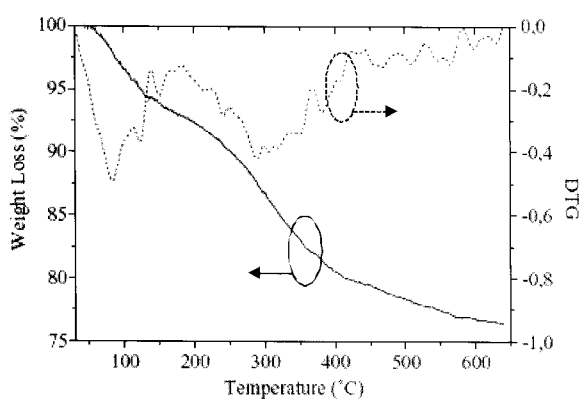


Fig. 2. IR spectra of prepared F:SnO<sub>2</sub> samples with various treatment temperatures.

(a)  $S_{80}$  (b)  $S_{400}$  (c)  $S_{450}$  (d)  $S_{500}$  (e)  $S_{550}$

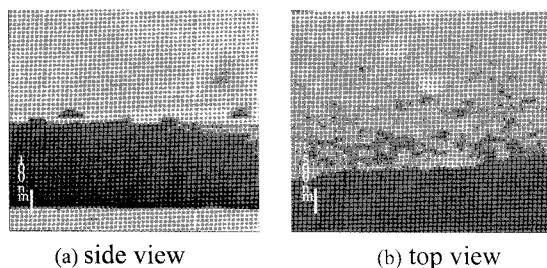
The TG-DTG plots recorded in air for the samples are displayed in Fig. 3. Three main mass losses of 6.5, 13.3 and 3.8 at 81, 289 and 490°C are observed between 50 and 650°C yielding a final residue of 76.0%. This value is in good agreement with the expected loss (24.7%) inferred from the formula SnF<sub>0.8</sub>(OH)<sub>0.8</sub>O<sub>1.1</sub>(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>0.2</sub> · 0.8H<sub>2</sub>O which may be proposed for  $S_{80}$  according to the elemental analysis data. It is worthwhile mentioning that the F/Sn atomic ratio has decreased in the molecular sol-gel precursor. The nature of the species present in  $S_{80}$  was then checked by TG-MS measurements. The main chemical species evolved are water (m/z=18), the

degradation products of pentan-2,4-dionato ligands ( $m/z=43$ : acetyl;  $m/z=58$ : acetone;  $m/z=60$ : acetic acid), carbon dioxide ( $m/z=44$ ) and fluorine ( $m/z=20$ : fluorhydric acid). The  $m/z$  here is defined as the mass-to-charge ratio. As shown in Fig. 3, the trends of the ion fragments are detected as a function of the temperature. The pyrolysis steps can therefore be rationalized as previously reported [14, 17]. In particular, fluorine is continuously released as HF from 250°C as soon as the loss of structural water starts. This is consistent with a hydrolysis of the Sn-F bond activated by high temperature.



**Fig. 3.** TG-DTG characteristics of prepared F:SnO<sub>2</sub> ( $S_{80}$ )

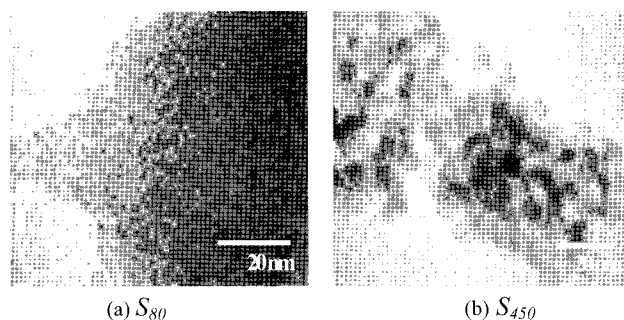
Fig. 4a-b show the SEM images of the prepared nanoporous SnO<sub>2</sub> films. Film of about 250 nm thickness is observed in the fractured cross-section of Fig. 4a. Also, the rough surfaces with rounded grains are apparent, and the grain size of 200-500 nm can be confirmed in Fig. 4b. In this figure, the porous structure of the films is not clear.



**Fig. 4.** SEM photographs of prepared F:SnO<sub>2</sub> films.

The example of TEM photographs of the xerogel  $S_{80}$  and the calcined samples are displayed in Fig. 5. It is clear from Fig. 4a that  $S_{80}$  has a “worm-hole” or “sponge” topology with numerous small pores (2-5 nm), this kind of texture being often reported for mesoporous metal oxides [18]. After calcination, this porous structure was replaced by a network of aggregated SnO<sub>2</sub> nanoparticles, the size of which rose from 5 nm to 10-12 nm (Fig. 5b) as the

temperature of thermal treatment was increased from 400 to 550°C. Consequently, the surface area of the SnO<sub>2</sub>-based materials is reduced upon thermal treatment, as confirmed by the nitrogen sorption measurements.



**Fig. 5.** Example of TEM photographs of the xerogel  $S_{80}$  and the calcined samples.

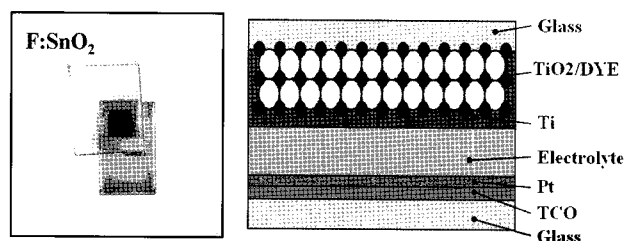
The BET surface area, total pore volume and mean pore size (BJH model) results are summarized in Table 1. The surface area of the xerogel  $S_{80}$  is rather high, 250 m<sup>2</sup>/g, and the total pore volume is of about 0.24 cm<sup>3</sup>/g. Calcination induces a strong decrease of the specific area without affecting the total pore volume value. Indeed, BET surface area is found to be 115 and 70 m<sup>2</sup>/g for  $S_{450}$  and  $S_{550}$ , respectively, and the total pore volume, 0.22 cm<sup>3</sup>/g, remains almost constant. After thermal treatment, the mean pore size diameter increases from 5 nm for  $S_{400}$  to 10 nm for  $S_{550}$ , an enormous change occurring between 450 and 550°C. It can be seen that this phenomenon is closely connected to the crystallization and sintering of SnO<sub>2</sub> particles.

**Table 1.** BET surface area, total pore volume and mean pore size of the samples

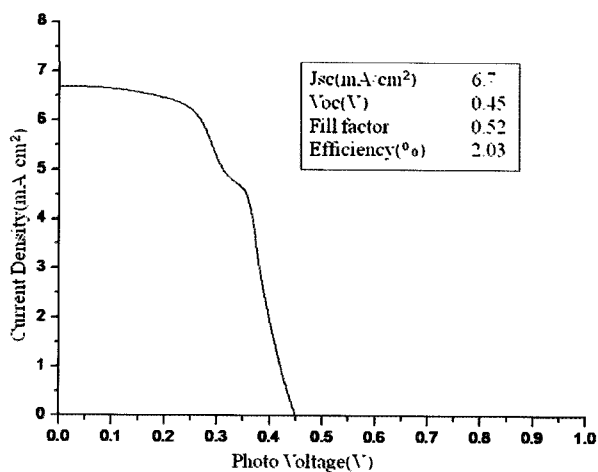
Sample	$S_{BET}$ (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Mean pore diameter (nm)
$S_{80}$	250	0.24	-
$S_{400}$	150	0.22	50
$S_{450}$	115	0.22	60
$S_{500}$	85	0.22	90
$S_{550}$	70	0.22	100

The synthesis of nanoporous F:SnO<sub>2</sub> materials in this experiment was used in dye sensitized solar cells (DSCs) sample. These DSCs was prepared and then irradiated with a Light Drive 1000 lamp through an infrared-

blocking filter. Fig. 6 shows the image of the prepared DSCs sample with nanoporous F:SnO<sub>2</sub> electrode (cell size: 5mm×5mm) and current-voltage characteristic of this sample. The photoelectric efficiency was calculated with respect to the solar spectra through a calibration of the Light Drive 1000 lamp with direct sunlight. It exhibits an energy conversion efficiency of 2.03 % at 100mW/cm<sup>2</sup> light intensity.



(a) Image of prepared F:SnO<sub>2</sub>-based DSCs sample



(b) Current-voltage characteristics

**Fig. 6.** DSCs sample with F:SnO<sub>2</sub> electrode and photovoltaic characteristics.

#### 4. Conclusion

The controlled hydrolysis of fluoro(2-methylbutan-2-oxy)di(pentan-2,4-dionato)tin followed by annealing at 400-550°C gave conductive nanoporous F:SnO<sub>2</sub> materials. Tuning of the annealing temperature enabled us to prepare materials with surface areas ranging from 70 to 150 m<sup>2</sup>/g, with an average pore size comprised of 5 and 10 nm and mean particle diameter ranging from 5 to 12 nm. The surface area of the SnO<sub>2</sub>-based materials was reduced upon thermal treatment as confirmed by the TEM and

BET surface measurement. It can be seen, from the result, that this phenomenon is closely connected to the crystallization and sintering of SnO<sub>2</sub> particles.

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