

## Supplementary Materials

### **The impact of thermal treatment on the structural, optical and electrochemical characteristics of tin sulfide films**

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#### **Characterization of thin tin sulfide films.**

A D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) that works at a tube voltage of 40 kV and tube current of 40 mA was used for X-ray diffraction (XRD) analysis. Obtained results as diffraction patterns were accounted for in a Bragg- Brentano geometry applying a quickly calculating 1-dimensional detector Bruker LynxEye. This is based on silicon strip technology. For filtering, the X-ray Ni 0.02 mm filter to repress Cu-K $\beta$  radiation. Step scan include the angular range of 5–70° (2 $\theta$ ) at a scan speed of 6° 1/min using a two-theta / theta coupled scan way. From the X-ray diffraction patterns the most intensive peaks of detected compounds which did not overly the peaks of other compounds were used to calculate crystallites size. Therefore, DIFFRAC.SUITE EVA v. 4.5 software was used for this purpose.

Raman imaging of the film on FTO glass samples was performed with a Horiba Jobin-Yvon LabRAM (Longjumeau, France) system utilizing a 532 nm, 40 mW Nd:YAG laser, which was focused on the sample with an Olympus BX-40 optical microscope, where a magnification of 20x was used. If the laser was used without neutral density filter, the chemical properties of the material

changed due to the strong laser light, so spectral maps were obtained with filter with 10% transparency, in this case results were reproducible. Chemical imaging was performed by moving the sample by an automatic, programmed stage before each spectral acquisition. In this way, a 0.4 x 0.4 mm<sup>2</sup> area was covered in steps of 20 µm, meaning that a total of 21 x 21 = 441 spectra were collected. Each spectrum was recorded with an acquisition time of 60 s and 2 spectra were averaged at each location, therefore the total time required to measure a sample was approximately 14.7 h. The spectral region of 47–600 cm<sup>-1</sup> was covered.

Data processing was performed in MATLAB release 9.13 (Mathworks, Natick, MA, USA) with PLS\_Toolbox 8.8.1 (Eigenvector Research, Manson, WA, USA). To demonstrate our findings in these samples, the averages of 441 collected spectra for each sample were calculated. Spectra were preprocessed before, by Savitzky-Golay smoothing (2nd order, 11 pt window) and baseline correction with Automatic Whittaker Filter (asymmetry=0.001,  $\lambda = 5000$ ).

XPS measurements were conducted using a VG ESCA3 MkII electron spectrometer with a base pressure exceeding 10<sup>-9</sup> mbar. Excitation of electrons was achieved using Al K $\alpha$  radiation. Electron energy analysis was performed using a hemispherical analyzer set to a constant pass energy of 20 eV. Calibration of the spectra was carried out by aligning the primary feature of the C 1s region to a binding energy of 284.8 eV. Surface atomic content was determined assuming a homogeneous distribution of atoms and utilizing Scofield photoionization cross-section. XPS analyses were carried out at a 45° angle to the sample surface. Typically, the information depth of XPS is approximately 5 nm. The binding energies of all peaks were adjusted using the C 1s region with a binding energy of 284.8 eV, which corresponds to random carbon and accounts for charge compensation by the flood gun associated with the spectrophotometer.

The morphology of the tin sulfide films was characterized using a high-resolution field emission scanning electron microscope SU-70 (Hitachi, Japan) (FE-SEM).

Ultraviolet and visible light (UV-Vis) spectroscopy has been used to study optical properties. A Perkin Elmer Lambda 35 UV-Vis spectrometer was used with the Labsphere RSA-PE-20 diffuse reflection sphere in the range of 400–900 nm was used to record optical absorption spectra at room temperature.

Tauc's plot was used to calculate the bandgap energy of thin tin sulfide films:

$$\alpha h\nu = B(h\nu - E_g)^n$$

where B – the parameter that depends on the transition chance, n – the value that depends on the type of transition (n = 1/2, 2/3, 3 for allowed indirect, allowed direct, forbidden direct and forbidden indirect transition, respectively) [30].  $\alpha$  is possible to calculate using the formula:

$$\alpha = \frac{\ln 10 \times A}{d}, \text{ where } A \text{ is absorbance, } d - \text{layer thickness.}$$

The bandgap energies were calculated using the plot of  $(\alpha h\nu)^n$  versus the photon energy  $h\nu$ . The extrapolated linear part of the plot, when  $(\alpha h\nu)^n=0$  until it crosses the photon energy axis ( $A=0$ ), so  $E_g = h\nu$ .

All electrochemical experiments were conducted using an SP-150 potentiostat/galvanostat (Bio-Logic, France). A three-electrode system consisting of a platinum wire as a counter electrode, Ag,AgCl|KCl(sat) as a reference electrode and films on FTO glass as working electrodes were employed. All experimental data were collected and analyzed with EC-Lab® V10.39 software. Cyclic voltammograms (CV) were recorded in 0.1 M NaCl solution in the potential range of –1 V to +1 V. The optimal scan rate of 20 mV s<sup>-1</sup> was selected. Each film was scanned ten times, and only the last cycle was introduced into comparison and calculations. The galvanostatic charge-discharge (GCD) behavior was examined at 1 A g<sup>-1</sup> specific current in 0.1 M NaCl solution.

The energetic parameters – specific capacitance ( $SC$ , F g<sup>-1</sup>), specific energy ( $SE$ , Wh kg<sup>-1</sup>) and specific power ( $SP$ , W kg<sup>-1</sup>) – were calculated according to the following equations [33]:

$$SC = \frac{I_{\text{appl}} \times t_D}{\Delta V \times m}$$

$$SE = \frac{0.5 \times SC \times \Delta V^2}{3.6}$$

$$SP = \frac{3600 \times SE}{t_D}$$

Where  $I_{\text{appl}}$  is the applied current (A),  $t_D$  is the discharge time (s),  $\Delta V$  is the potential window (V), and  $m$  is the mass of the active substance (g).

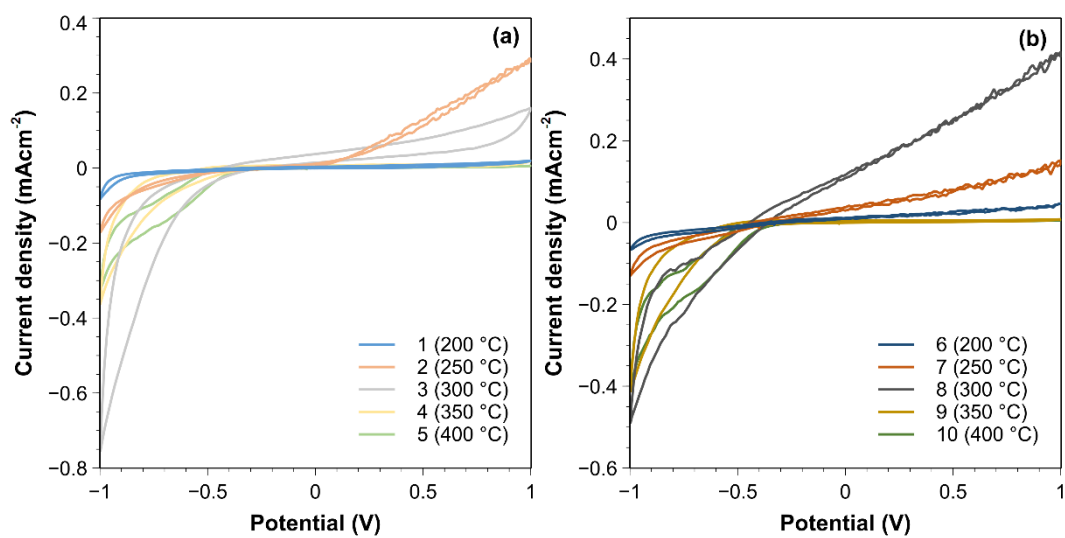


Figure. S1. CV curves of the tin sulfide coatings synthesized with 0.8 g of ascorbic acid (a) or 1.0 g (b) and annealed at different temperatures. Supporting electrolyte – 0.1 M NaCl