### **Electronic Supplementary Information**

### Tuning the deposition parameters for optimizing the faradaic and nonfaradaic electrochemical performance of nanowire array-shaped ITO electrodes prepared by electron beam evaporation

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## 1. SEM images of the nanostructured electrodes prepared at several substrate temperatures

**Figure S1.** SEM images of nanostructured ITO electrodes prepared by electron beam evaporation, with substrate temperatures of (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C. In the latter image, a representative 'seed' and 'stick' appear circled and outlined, respectively.

The self-catalytic VLS growth occurs from "seeds" that constitute regions offering high probabilities for the material to accumulate, inducing the nanostructuration appreciated in the SEM micrographs. Let us consider the substrate as a region activated by catalyst drops (the In-Sn alloy). Atomic or molecular particles of the semiconductor raw target material impact the catalyst drops either from an external flux at an arbitrary angle from the surface or by diffusion from the surface. Nanowire growth occurs by supersaturation of the catalyst drops with the flux material: the semiconductor is dissolved in the drop and the crystallization occurs at the drop-material interface<sup>1</sup>. A proof of the self-catalytic VLS growth method can be assessed again from the images shown in Figure S1. Indeed, if we take a careful look at the shape of the nanowires, we observe that although there are different lengths and widths, in all cases the aforementioned "seeds" are present at the tip of the whisker. This is indicative of the growth process for the nanostructures. Very precise compositional studies were conducted elsewhere<sup>2</sup>, showing by transmission electron microscopy (TEM) that the composition and crystallinity at the tips is essentially the same of the sticks'. Moreover, the stoichiometry of the target material is also conserved, altogether accounting for the accuracy and degree of precision this method provides for nanowire fabrication.

- A. G. Nastovjak, I. G. Neizvestny and N. L. Shwartz, *Pure Appl. Chem.*, 2010, 82, 2017–2025.
- 2 R. R. Kumar, K. N. Rao, K. Rajanna and A. R. Phani, *Mater. Res. Bull.*, 2014, **52**, 167–176.

2. SEM image of a thin ITO film prepared at 100 °C



**Figure S2.** SEM image of a thin ITO film prepared by electron beam evaporation at a substrate temperature of 100 °C. No nanowhiskers or other structures can be appreciated.

3. Transparency of ITO electrodes prepared at several temperatures



Figure S3. Transparency of the as-deposited nanostructured ITO electrodes at naked eye.

4. Faradaic cyclic voltammetry



**Figure S4.** Faradaic cyclic voltammetry of ITO electrodes prepared at (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C. The cycles were taken at scan rates of 10, 25, 50, 75, 150, 250, 350, 500 mV s<sup>-1</sup> (increasing order in the figures).

#### 5. Non-faradaic cyclic voltammetry



**Figure S5.** Non-faradaic cyclic voltammetry of ITO electrodes prepared at (a) 200 °C, (b) 300 °C, (c) 400 °C and (d) 500 °C. The cycles were taken at scan rates of 10, 25, 50, 75, 100, 300, 500 mV s<sup>-1</sup> (increasing order in the figures).