

Electrosynthesized porous tin oxide film for gas sensors applications

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Summary:

Herein, the electrochemical synthesis of porous tin oxide (SnO_2) semiconducting film is demonstrated for application in gas sensors to detect redox gases. The application of a negative electrode potential in a strong acidic precursor solution induces a series of chemical and electrochemical reactions. The interplay of these reactions produces a porous, chemically pure and polycrystalline SnO_2 film over the gas sensor's electrodes. The preliminary tests under different redox gases confirm the enhancement in the sensitivity of the SnO_2 sensors compared to a reference SnO_2 based gas sensors.

Keywords: Metal oxides, Porous materials, Electrosynthesis, gas sensors, Healthcare

Background, Motivation and Objective

There is a growing research interests in developing an electronic nose for breath analysis of a person for the premature diagnostic of disease^{1, 2}. Indeed, the human breath contains a complex mixture of oxidizing, reducing and volatile organic compounds (VOCs), which composition and concentrations change depending on the occurrence of a disease. For instance, a kidney infection shoots up ammonia (NH_3) concentration in the breath more than 14 times, while early-stage asthma increases the concentration of nitric oxide (NO) 4 times in the breath compare to a breath of a healthy person^{3, 4}. Such disease biomarkers gases have been conventionally detected using gas sensors based on metal oxides, like tin oxides (SnO_2), which are abundant and inexpensive. Current approach of using these materials in gas sensors comprise synthesis of powder by hydrothermal method followed by processing of the corresponding ink on the sensor electrodes into thin film by screen printing or similar solution casting methods. However, the morphologies of such metal oxides films are often compact and that reduces their sensitivity towards the redox gases detection. On the other hand, the detection benchmarks for the disease biomarkers in the breath is often in ppb range, necessitating drastic improvement in the sensitivity of metal oxide-based sensors. In this endeavor, we report an electrosynthesis approach of one step synthesis and deposition of porous film of SnO_2 onto gas sensor electrodes, which

is rapid, precise and well-controlled in terms of thickness and porosity.

Description of the New Method

The key novelty of the presented work is the innovative electrochemical methodology, in which *in situ* generated hydrogen bubbles provides a dynamic template for the pores evolution in simultaneously forming SnO_2 deposit. The Dynamic Hydrogen Bubble Template (DHBT) method^{5, 6} has been previously explored only for the metal film deposition but never for the metal oxide film. The fine control of the electrochemical conditions could produce a hierarchical porosity in the SnO_2 film deposited over the gas sensors electrodes.

Results

The electrosynthesis is performed by electroreduction at a fixed potential in a precursor solution containing a tin salt, a source of oxygen and a proton source. Notably, the presence of the proton source causes hydrogen evolution reaction at the electrode, producing bubbles at the electrode surface and that behave as a soft dynamic template^[2] to induce porosity in the metal oxide deposit. We have modulated the electrosynthesis potential, time and temperature to tune the porosity and microstructures of the SnO_2 porous film. The preliminary results have demonstrated the production of a porous film of SnO_2 (Figure 1a), having multiplicity of pore sizes. Such hierarchical porous morphology is a characteristic feature of DHBT deposition. The microstructure, upon investigation with X-ray diffraction (XRD) exhibits reflection peaks characteristic of rutile or

cassiterite phase of SnO_2 . The surface analysis of the film by X-ray photoelectron spectroscopy (XPS) shows characteristic peaks associated to Sn^{4+} oxidation state. The porous coating is of high chemical purity and is devoid of any potential metallic tin contamination, as confirmed by XPS analysis. The electrochemical characterizations of the porous SnO_2 coating further revealed hindered electron transfer reaction of a redox probe $\text{K}_3[\text{Fe}(\text{CN})_6]$ compared to a conventional gold electrode, which exhibits well-defined redox peaks, highlighting low conductivity of the oxide film. Optimization of the electrosynthesis parameters, evaluation of the associated mechanism and application of porous SnO_2 film in redox gases sensing are the scope of our ongoing activities.

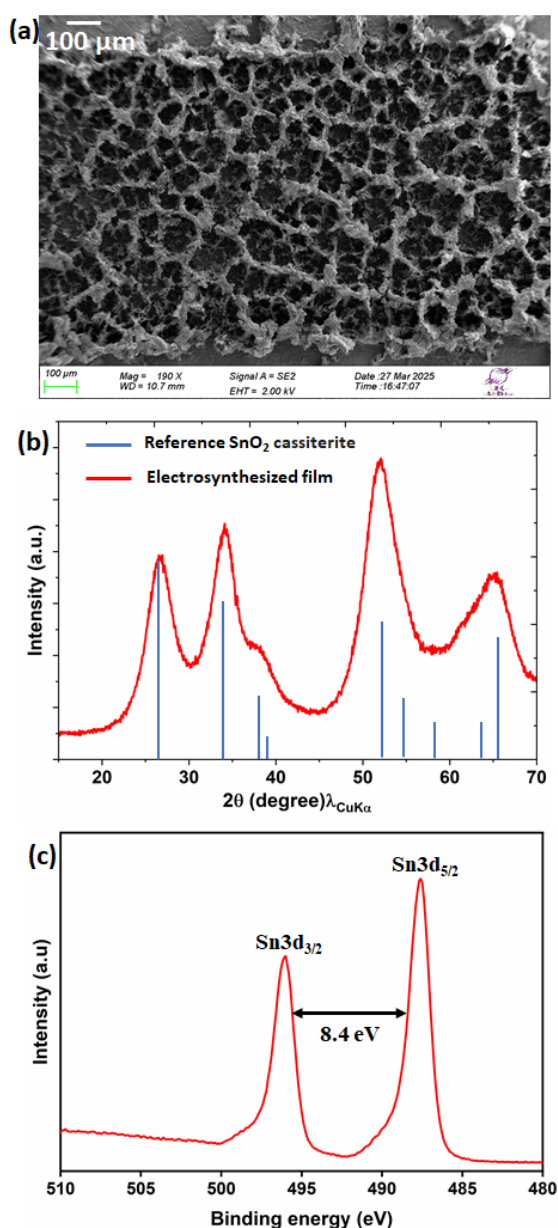


Fig. 1. SEM image (a), XRD profile (b) and XPS high resolution spectrum (c) of SnO_2 film.

References

- [1] I. Mondal, A. Zoabi, H. Haick *Adv. Funct. Mater.* 2025, 35, 2425193.
- [2] M. Hijazi, M. Rieu, V. Stambouli, G. Tournier, J.-P. Viricelle, C. Pijolat *Sensors and Actuators B: Chemical*. 2018, 256, 440-447.
- [3] G. Konvalina, H. Haick *Acc. Chem. Res.* 2014, 47, 66-76.
- [4] A. Haccuria, A. Michils, S. Michiels, A. Van Muylem *Journal of Allergy and Clinical Immunology*. 2014, 134, 554-559.
- [5] B. J. Plowman, L. A. Jones, S. K. Bhargava *Chemical Communications*. 2015, 51, 4331-4346.
- [6] A. Kumar, J. Lüder, M. Bertotti, K. Araki, F. Montoro, F. Herbst, R. Meunier-Prest, L. Angnes, M. Bouvet, J. Bettini, J. M. Gonçalves *ACS Applied Nano Materials*. 2024, 7, 7213-7225.