



Electrochemistry and Spectroelectrochemistry with Electrospun Indium Tin Oxide Nanofibers



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ABSTRACT

In this work, Indium tin oxide (ITO) nanofiber materials have been prepared and subsequently used for electrochemical and spectroelectrochemical analysis. Nanofibers have been electrospun from a suspension of polyvinylpyrrolidone (PVP) and indium and tin precursors with a ratio Sn/In = 0.16. Their diameter could be adjusted between 110 and 235 nm and the layer thickness was controlled between 12 and 120 μm . A calcination at 500 °C in air followed by a thermal treatment at 1000 °C under nitrogen atmosphere allowed to obtain conductive ITO nanofibers. XRD characterizations confirmed the successful transition of the starting material into indium tin oxide, showed the influence of the thermal treatment on grain size and provided some insight on their orientation. The electrochemical properties of the nanofibers have been characterized and optimized using dimethanolferrrocene as a model probe. This porous ITO electrode have been applied to the electroanalysis of ascorbic acid with a sensitivity of 1.04 mA mM⁻¹ cm⁻² and to spectroelectrochemistry using Prussian blue as model system.

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1. Introduction

Porous electrodes have been of interest for many years. Their main applications are supercapacitors, electrocatalysis and electroanalysis [1–3]. High electroactive surface area allows for improving the detection of analytes. Indeed, creating bigger area of contact between an electrode and a solution can enhance the sensitivity of the analytical method, i.e. by preconcentration of the analyte on the electrode material itself or on a deposited layer [4], and gives the opportunity to improve the detection selectivity, i.e. by lowering the detection potential of important analytes such as H₂O₂ or NADH [5].

In some situations, an electrochemical detection at porous electrodes can be advantageously combined with a spectroscopic detection [6–9]. In general, spectroelectrochemistry allows to analyze single and multiple electron-transfer processes and redox reactions [10] and authorizes a multimode selectivity beneficial for

the analytical chemistry [11,12]. A transparent material is however needed to perform spectroelectrochemical measurements through the electrode surface [12].

According to Cao et al. [13] the most often applied among the developed transparent materials are transparent conducting oxides (TCOs): indium-tin oxide (ITO), antimony-tin oxide (ATO) and fluorine-tin oxide (FTO). Additionally there are carbon materials like thin layers of graphene or PEDOT or carbon composites of transparent non-conductive polymers with conductive fillers. Of aforementioned materials the most commonly used is ITO. Their very low resistivity (10–50 Ωsq^{-1}) [13] and high transparency (80–95%) [13] have allowed commercial application of non-porous ITO thin films on a wide scale in touch screen devices [14,15].

ITO can also be prepared in a form of porous electrode and it can be obtained with different degrees of porosity that may suit different goals [16]. One popular group are mesoporous electrodes that offer big relative surface area (up to 200 m² g⁻¹) [17]. There exist a number of methods that allow deposition of thin, well-ordered mesoporous layers. The first group of such methods are vacuum methods like sputtering [18,19], glancing angle deposition [20,21], metalorganic chemical vapor deposition [22] or pulsed laser deposition [23]. Next group are wet and evaporation methods

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like spin coating [17,24–26], nanocrystal assembly [27,28], doctor blade [29,30], dip-coating [31,32], sol-gel deposition [25] and nanocasting [33]. As mentioned, resulting mesoporous layers have some advantages like high surface area but at the same time diffusion can be dampened and further functionalization is limited.

Another approach is to get a macroporous surface which despite having lower relative surface area possesses some advantages over mesoporous materials like a wider access to the internal surface and better mass transfer through the electrode. Additionally, after the deposition, if needed, they can be functionalized with meso- or microporous layers to maximize the specific surface area or to introduce catalytic activity [34,35]. One common way to obtain macroporous ITO layers is through templating using various procedures like electrochemically assisted deposition [36], self-assembly deposition [37] or electrophoretic deposition [38]. Another way to deposit macroporous ITO layers is electrospinning [39–47]. Compared to methods achieving macroporosity through templating, nanofiber films generated using electrospinning do not have the problem of narrow connections that the former often possess [48].

Electrospinning of ITO has been already performed using different setups, precursors (indium and tin salts or nanoparticles), solvents (water, methanol, DMF/ethanol mixture) and polymers (poly(vinyl alcohol), poly(ethylene oxide), polyvinylpyrrolidone) [39–47]. So far their application was tested in photovoltaic devices [39] or sensing of trimethylamine [43]. However, until now there was no investigation into electrochemical properties of electrospun ITO nanofiber layers despite their great potential. In this work we show the application of electrospun ITO nanofiber layers in electrochemistry and electroanalysis and we demonstrate its suitability for spectroelectrochemistry. Some key parameters of deposition and treatment for these specific applications have been optimized and the materials have been carefully characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques.

2. Experimental section

2.1. Chemicals

Indium(III) nitrate hydrate 99.99% was purchased from Alfa Aesar. Anhydrous tin(II) chloride 98% was obtained from Acros

Organics. Polyvinylpyrrolidone of average $M_w = 1,300,000$, tin(IV) chloride pentahydrate 98%, iron(III) chloride hexahydrate 98%, 1,1'-dimethanoferrocene 98% and N,N'-dimethylformamide 99.8% were purchased from Sigma Aldrich and ethanol absolute 99.9% was obtained from Carlo Erba. L (+) Ascorbic Acid 99.7% was a Merck product and potassium chloride 99% a Prolabo product. Hydrochloric acid 37% and potassium hexacyanoferrate(III) 99% were obtained from Fluka.

2.2. Preparation of the suspension

The suspension from which electrospinning was conducted was prepared as follows: 1.12 g of $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (ca. 186 mM) and 0.084 g of SnCl_2 (ca. 30 mM) were dissolved in mixture of 8.1 mL of ethanol and 6.75 mL of dimethylformamide. Then, the mixture was stirred 3 hours until complete dissolution of the salts. Afterwards 1.2 g of polyvinylpyrrolidone (PVP) was added and again the stirring continued for 2 h until complete dissolution.

2.3. Electrospinning experiment

Standard horizontal setup was used for electrospinning (Fig. 1). In short, KdScientific syringe pump was used to deliver solution from 5 mL syringe through a needle 21 G with outer diameter of 0.8 mm. Flow rate imposed by pump was optimized and then kept at $2 \mu\text{L min}^{-1}$ during all experiments. Ahead was placed a stainless steel collector plate with dimensions of $28 \text{ cm} \times 28 \text{ cm}$. The distance between the needle tip and the collector plate was kept at 12.5 cm. High voltage power supply by Iseg was used to apply potential, with negative pole being connected to the needle. Voltage applied was 10 kV in all experiments unless stated otherwise. Collector plate was connected to the ground (0 V) hence the resulting potential of electrospinning is equal to voltage applied throughout all the experiments. Time of deposition varied between 5 to 40 minutes. After electrospinning procedure, the electrospun matter was stripped off of the steel plate collector and became a free-standing mat.

2.4. Post-treatment

Nanofiber mats were transferred to oven to undergo calcination in 500°C in air for 1 h (with a temperature ramp of 100°C h^{-1}).

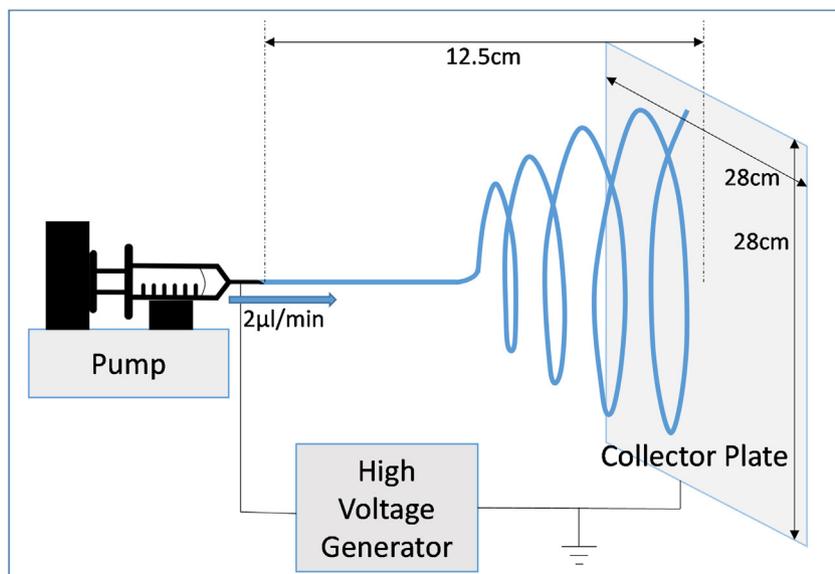


Fig. 1. Electrospinning configuration used for deposition of ITO nanofiber layers.

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