



## Research Paper

# Evaluation of transferable TiO<sub>2</sub> nanotube membranes as electrocatalyst support for methanol photoelectrooxidation



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## ABSTRACT

TiO<sub>2</sub> nanotube membranes (TNM) were synthesized, separated (by electrochemical anodization) and modified with Pt-Ru electrocatalyst to assess their photoelectrocatalytic activity towards methanol (MeOH) oxidation. The feasibility of use of these composite materials was evaluated in different supports to observe the development of the electrochemical responses as a function of the nature of the electrical collecting substrate. The results suggested that, while the Pt-Ru decorated TMN present photoelectrocatalytic activity, the electrical contact in the back might be the limiting step in current collection. Such findings were demonstrated by performing scanning electrochemical microscopy SECM over the surface of the TNMs, where methanol was oxidized in the microelectrode tip of the SECM. This approach corroborated the suitability of TNMs to be modified with an electrocatalyst and its application in current technology such as microfluidic fuel cells.

## 1. Introduction

Among the various nanomaterials, TiO<sub>2</sub> nanotubes (NTs) are regarded as one of the most promising candidates for energy and environmental applications holding great potential due to its innocuity, low-cost, enhanced surface hydrophilicity and excellent physical and chemical stability [1–3]. Their high photocatalytic activity of NTs results from their specific surface area, crystallinity and porous structure [4,5]. Due to its bandgap, NTs require UV light irradiation to generate photo-induced charge carriers (electron-hole pairs) and such characteristic has been used in several fields such as alternative energy technologies, photocatalysis, solar cells, gas sensing and photo-electrochemical cells [6]. To properly profit from the advantages of this morphology in photoelectrocatalytic applications, the substrate-electrode (S.E.) configuration should be used as it is the most efficient in such systems. However, the nature of the synthesis process of NTs prevents from using the S.E. configuration since they are strongly attached to the metallic Ti substrate which difficulty their assessment in this technology.

With the current surface engineering development, cutting-edge morphologies in the nanometer scale can be tailored for specific applications. As an electrocatalyst support, TiO<sub>2</sub> has been used in the electrodes for microfluidic fuel cells to improve the performance of

noble metal electrocatalyst like Pt and Pd, by modifying the electronic surface properties [7–9]. Such cells have evolved to the point of producing flexible assemblies, thus the possibility of incorporating a flexible TiO<sub>2</sub> membrane (TNM) in these systems represents a promising alternative to design next-gen devices that can be adapted to complicated topologies, such as in textiles, on-skin sensors and medical applications [10–14].

However, to the best of our knowledge, the reports on the preparation of TNM modified with electrocatalytic materials are very scarce; as a structured photoelectrocatalyst, to study its activity towards methanol electrooxidation. Therefore, in this work, we report the synthesis and characterization of transferable TNMs modified with Pt-Ru electrocatalyst; The photocatalytic activity towards methanol electrooxidation was evaluated under UV light by scanning electrochemical microscopy (SECM) technique to verify the photo-generated holes.

## 2. Experimental setup

## 2.1. Preparation of photocatalytic supports

## 2.1.1. Synthesis of TNM

The preparation technique for the TNM was performed by electrochemical anodization [15]. Metallic titanium sheets (99% purity,

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thickness 0.127 mm, Alfa-Aesar) were sand-paper polished. Subsequently, they were sonicated for 15 min in ethanol, acetone (Sigma-Aldrich) and distilled water successively and then dried under nitrogen gas flow (99.999, Praxair). Once cleaned, they were immersed in an acrylic cell in a 0.1 M  $\text{NH}_4\text{F}$  ethylene-glycol (96% purity, Alfa-Aesar) based electrolyte with 2% w/w deionized water. A two-electrode arrangement was used, with a steel sheet as a counter-electrode and placed at 2.5 cm from the working electrode. The potential imposed ( $E_1$ ) between both electrodes was 60 V (BK Precision model 9184) and NTs-TiO<sub>2</sub> were grown at different anodizing times ( $t_{a1}$ ) of 0.5, 1, and 4 h.

To induce the crystallinity of the nanotubes to their phase with better electrical conduction properties (anatase), a heat treatment was applied in a muffle (Tube Furnace 21 100) for 2 h at 450 °C, with a temperature ramp of 10 °C/min under air atmosphere.

### 2.1.2. Detachment of TNM

The easy and complete detachment of nanotubes was achieved with the application of a second anodizing process after the heat treatment.

A potential of 160 V ( $E_2$ ) for 30 s ( $t_{a2}$ ) was imposed on all the anodes obtained at different times. After the NTs were embrittled, the anodized sheet was rinsed in EtOH and then in water for 15 min. Finally, with a slight mechanical stress it is possible to separate the membrane (See Fig. S1 in supplementary information).

### 2.1.3. Transfer of membranes on ITO glass

The transfer of the membranes was performed using ITO glass as a conductive substrate and Nafion (5 wt.% Sigma Aldrich) as an adhesive, aiming to approximate the system to the methods used in the fuel cells to evaluate the catalytic inks by the drop-cast technique, being a method little explored to achieve the electrical interconnection between the membrane and the conductive support, where contact is generally achieved using sintered TiO<sub>2</sub> nanoparticles, which subsequently require sintering to create adequate electrical continuity, the need to reach high temperatures to sinter the material precludes its application in substrates that are not thermally resistant. The membranes can be transferred to other conductive and flexible supports such as ITO/PET and an interesting alternative is how to develop transparent and flexible electrodes without the need for previous thermal treatments to achieve the interconnection between the membrane and the substrate conductor.

### 2.1.4. Deposition of Pt-Ru on TNM

The depositions of the materials achieved with Nafion (5 wt.% Sigma Aldrich) by the drop-cast technique. The ink composition had a ratio of 120  $\mu\text{l}$  of isopropanol and 14  $\mu\text{l}$  of Nafion per milligram of catalyst. The catalyst evaluated was Pt-Ru/XC-72 (Johnson Matthey, HiSPEC 5000) and 2  $\mu\text{l}$  of ink was deposited.

## 2.2. Materials characterization

### 2.2.1. Physicochemical characterization of the electrodes

The morphology and microstructure of the samples were examined by Scanning Electron Microscope (SEM, JEOL/JSM-6510LV) equipped with a detector for dispersive energy spectroscopy (Bruker, XFlash 6I10). The elemental composition was analysed by an energy-dispersion spectroscopy (EDS, Oxford link system) analyzer, which was equipped to the SEM. X-ray Photoelectron Spectroscopy studies (XPS) studies allowed to complement the information of the elements present, of the chemistry, organization and morphology of the surface with a 3 Monochromatic Magics Thermo Scientifics, (model K-Alpha + Surface analysis). To confirm the identity of the formed film and corroborate the effectiveness of the heat treatment to induce crystallinity in them, Raman spectroscopy was performed with a Thermo Nicolet model DXR equipped with a 780 nm laser and a 12x optical microscope, the spectra were obtained with a power of 12 mW  $\text{cm}^{-2}$  and a grid aperture of the spectrophotometer of 50  $\mu\text{m}$ . UV–vis diffuse reflectance spectra (DRS)

of the samples were recorded on a UV–vis spectrophotometer (USB2 + F00099 Ocean Optics device), using Backscattering Probe, with a lamp of 180.50–880.52 nm. X-Ray Diffraction (XRD) pattern of the samples were recorded by X-ray diffraction spectrometer with Cu  $K\alpha$  radiation (D8-advance, Bruker-AXS, D8 Advance).

### 2.2.2. Photoelectrochemical characterization of TNM and TNM modified with Pt-Ru (Pt-Ru/TNM)

2.2.2.1. Cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA). To study its electrochemical behaviour and photocatalytic activity towards methanol electrooxidation, an electrochemical cell (Fig. 6a) equipped with a quartz window was used.

Electrochemical measurements were performed on different media (0.5 M  $\text{H}_2\text{SO}_4$  and 0.5 M MeOH/0.5 M  $\text{H}_2\text{SO}_4$ ) bubbled with  $\text{N}_2$  (99,999, Praxair) at room temperature using an experimental arrangement of three electrodes. In these experiments, the reference electrode and counter electrode were an Ag|AgCl and a graphite bar, respectively. The electrocatalytic properties to methanol oxidation were evaluated through CV with several sweeps between potentials of  $-0.35$  to 0.8 V vs NHE at a scan rate of 50  $\text{mV s}^{-1}$ . The LSV were performed in the same range of potentials as the CV but at 5  $\text{mV s}^{-1}$ , while the CA were run at 0.2 V vs Ag|AgCl. The evaluation was performed under darkness and UV light, illuminating with a 365 nm LED lamp with an effective irradiation power ( $I_0$ ) of 22.4  $\text{mW cm}^{-2}$  at the working electrode distance.

### 2.3. Evaluation Pt-Ru/TNM by scanning electrochemical microscopy

The TNM was evaluated by this technique, using a scanning electrochemical microscope (Biologic, ac-SECM/SECM470, in SG/TC mode) and the images were obtained by means of the software MIRA. A four-electrode cell consisting in a graphite rod as auxiliary electrode, reference electrode of Ag|AgCl, a 25  $\mu\text{m}$  diameter platinum ultramicroelectrode (UME) and a gold electrode (diameter: 5.3 mm) as working electrode using a 0.5 M methanol in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte. 2  $\mu\text{l}$  of Nafion were applied to the surface of working electrode to bind it onto the TiO<sub>2</sub> membrane. The membrane was modified with an ink consisting of Pt-Ru/XC-72 (Johnson Matthey, HiSPEC 5000) dispersed in a solution isopropyl alcohol-water (1:3 ratio), and 14  $\mu\text{l}$  of Nafion per mg by drop-cast deposition. Substrate generation and tip collection (SG/TC) mode of SECM was used, applying a potential of 0.2 V Ag|AgCl in the membrane, where the oxidation of methanol starts and 0.6 V vs Ag|AgCl in the platinum electrode for the oxidation of the generated formic acid.

## 3. Results and discussion

### 3.1. Physicochemical characterization TNM

The yellow coloration of the membrane increased with anodizing time and becomes more intense, which is associated with a greater incorporation of fluorides, but still allows the passage of light with ease (Fig. 1a–c). In Fig. 1, the SEM images also show well-defined NTs-TiO<sub>2</sub> arrangements with a regular and ordered structure over the entire anodized area. These structures had an average outer diameter of 84 nm and the total length of the nanotubes varies depending on the applied anodizing time ( $t_{a1}$ ), obtaining nanotubes of 5, 13 and 31  $\mu\text{m}$  in length for 0.5, 1 and 4 h respectively.

The samples produced with  $t_{a1} = 4$  h evidenced the presence of a light layer on top of the nanotubes. At this condition, the lower concentration of water changes the stoichiometric conditions giving rise to Ti complexes that precipitate on the surface, both conditions being direct consequences of an increase in anodizing time. The water content in the organic electrolyte is a necessary parameter since it requires  $\text{O}^{2-}$  and  $\text{H}^+$  for the growth and dissolution of the nanotubes and these ions come from water. The presence of this layer of precipitates on the

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