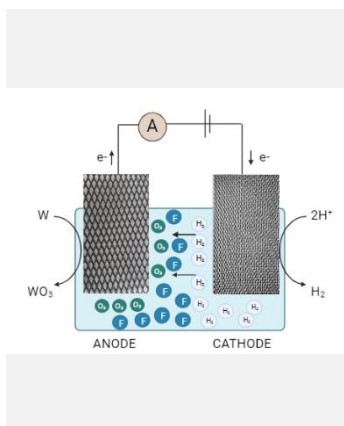


Determination of photoelectrochemical properties of nanostructured tungsten trioxide electrodes

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This work describes the investigation of two different methodologies for the synthesis of well-aligned WO_3 films, using the technique of electrochemical anodization in fluorinated electrolyte bases. The nanostructures of anodic tungsten trioxide (WO_3) were successfully synthesized by anodizing a W sheet at 40 V in a bath with an electrolyte composed of 1 M sodium sulfate (Na_2SO_4) and 0.7% by weight of ammonium fluoride (NH_4F), and at 60 V in a bath with an electrolyte composed of 0.15 M NaF. Both methodologies were investigated concerning the effect of electrochemical anodization times on the mechanism of the WO_3 nanostructure formation, as well as its photoelectrocatalytic properties. The high photocurrent density was obtained for the electrode anodized for 120 min. The amperometric curves were obtained by on/off cycles using an applied potential of +1.0 V, in 0.1 mol L^{-1} Na_2SO_4 electrolyte. This work contributes to the understanding of the nanotubular structure connected with the photoelectrocatalytic efficiency of WO_3 .

Introduction

Although the literature presents some references on the optimization of the geometric characteristics of the regular anode [1][2] the discussion about the nanotubular structure connected with the photoelectrocatalytic efficiency of WO_3 is still limited. Therefore, studies that seek to understand and customize the length, pore size, wall thickness of the nanopores, and their photoelectrocatalytic efficiency are of great importance [3]

WO_3 films have characteristics that make them suitable to be used as electrochromic layers in smart windows [4]. Many researches focus on the formation of a high active surface area of WO_3 nanostructures for use in electrochromic applications [5]. However, there is a consensus about the difficulty in obtaining a uniform and well-aligned growth of the WO_3 nanostructure related to good photoelectrochemical efficiency, usually focusing on the morphological process of the WO_3 [6].

In this work, we present the study of two different methodologies for the formation of well-aligned WO_3 films, using the technique of electrochemical anodization in fluorinated electrolyte bases. We investigated the effect of electrochemical anodization times, potential and supporting electrolyte type on the formation mechanism of the anodic nanostructure of WO_3 , as well as its photoelectrocatalytic properties.

Material and Methods

A high purity (99.95% purity with 0.2 mm thickness) tungsten (W) sheet was used for anodization. Briefly, the W sheet was pre-polished and washed in an ultrasonic bath for 5 min in acetone followed by isopropanol and water, and dried with N_2 . For the anodization, a conventional two-electrode cell with a W plate (1×1 cm) and a platinum grid was used as a working electrode and counter-electrode, respectively. Two methodologies were

used for the anodization process, where in methodology 1 the electrolyte is composed of 1 mol L^{-1} sodium sulfate (Na_2SO_4) + 0.7% ammonium fluoride (NH_4F), the applied potential was 40 V with a scan rate of 1 V/s [7]. In the present study, several anodization times (15 min (A1), 30 min (A2) and 60 min (A3)) were carried out to investigate the photoelectrochemical efficiency of WO_3 . In methodology 2 the electrolyte composed of 0.15 M NaF was used at 60 V with a scan rate of 2 V / 30 s, for 2 h (B) [8].

The morphology, structure and chemical composition of the WO_3 nanostructures were characterized by high-resolution scanning electron microscopy (FEG-SEM) (JOEL models JSM-7500-F and JSM-7401-F) equipped with energy dispersive X-ray analysis (EDX), X-ray diffractometry (XRD) using a Bruker D2 PHASER diffractometer with $\text{Cu K}\alpha$ radiation. Band gap values were obtained by diffuse reflectance using a PerkinElmer Lambda 1050 spectrometer. The photoelectrocatalytic activity of the formed WO_3 nanostructure was evaluated by electroanalytical techniques, such as linear sweep voltammetry (SLV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), using a conventional three-electrode anodization electrochemical cell with WO_3 nanotubes as working electrode, platinum rod as counter-electrode and Ag/AgCl as the reference electrode.

Results and Discussion

The evaluation of the photoelectrochemical performance of WO_3 for the different as-prepared samples A1, A2, A3, and B is presented in Figures 1a and b, recording the photocurrent values generated for each catalyst. In Fig. 1a, the curves show as expected an increase in photocurrent density along with the increase of the electric potential, with a higher photocurrent density for electrode B, reaching 2.3 ± 0.023 mA cm^{-2} , 60% higher than that obtained for A1, and 21% higher than A2. Fig. 1b clearly

shows the differences in the photoresponses obtained for each as-prepared semiconductor at an applied potential of +1.0 V, under a solar light simulator (100 mW cm⁻²). The results presented in Figure b are consistent with the photocurrent presented in Fig. 1a.

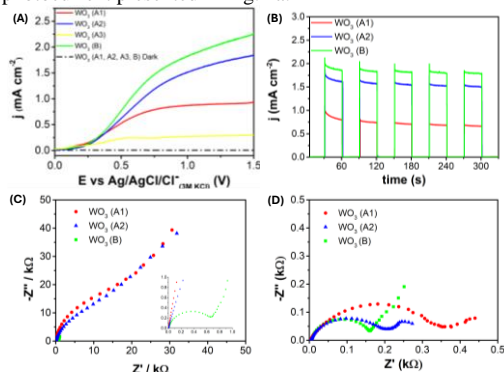


Fig. 1 (a) Polarization curve at 10 mV s⁻¹ with Xe (300 W) irradiation. (b) Amperometric curves on/off 30 s. (c) Nyquist diagrams under dark. (d) Nyquist diagrams in the presence of light (100mW cm⁻²). Measurements were performed in 0.1 mol L⁻¹ Na₂SO₄.

Furthermore, the analysis of the response shape of the amperometric curve indicates that the on/off cycle of the light photoexcitation in the electrode (Figure 1b) showed good recovery which is a desirable attribute for an electrode with repeatability and good photoelectrochemical efficiency, thus ensuring high efficiency of photocurrent generation and interruption. These data validated the optimization to improve the photoelectrocatalytic properties of the electrode.

The obtained Nyquist diagrams are shown in Figure 1c and d. In Fig. 1c, the diagram in red and blue (A1 and A2) shows similar high Rct values, while the diagram in green (B) which is better represented in the inset of Figure 1c shows Rct values lower than A2 and A1, indicating that the electrode B has excellent charge transfer through the interface between the electrode surface and the

Conclusions

The formation of WO₃ nanopores is attributed to the presence of tungsten fluoride complex ions which induces chemical dissolution to enlarge and deepen the pores and, eventually, transform it into nanotubes. The complete transformation of the W sheet into one-dimensional WO₃ well organized nanopores can be achieved with high crystallinity, better photocatalytic response, and low resistance after 120 min of anodization under 0.15 M NaF supporting electrolyte. This methodology has shown to be a good strategy to generate high photocurrent under visible light conditions. Furthermore, it was observed a decrease in charge transfer resistance by EIS analysis indicating that the electrode has excellent charge transfer rate across the interface between the electrode surface and the supporting electrolyte.

Acknowledgments

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electrolyte. Fig. 1d shows the Nyquist diagrams obtained for the systems under solar light with the aid of a 300 W Xe Xenon lamp with 100 mW cm⁻² of irradiation. Under light incidence the reduction in the Rct of the electrode B is more accentuated compared with A1 and reaching a similar behavior of electrode A2.

The use of energy-dispersive X-ray spectroscopy (EDX) analysis confirmed the presence of the main elements constituting the WO₃ electrode (data not shown). The WO₃ film presented a highly crystalline phase, as confirmed by X-ray diffractograms for the W foil before and after the formation of the WO₃ film (Fig. 2(a)). The peaks at $2\theta = 40.2^\circ$, 58.2° and 73.2° were characteristic of metallic tungsten (PDF00-004-0806). After film formation, there was a cluster of peaks ($2\theta = 23.1^\circ$, 23.5° , 24.3° , 33.2° , 33.5° , and 34.1°) characteristic of WO₃ in the monoclinic form (PDF00-043-1035).

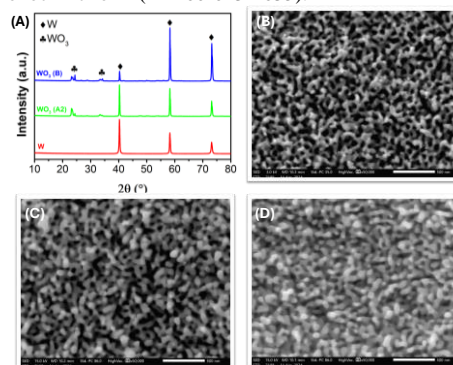


Fig. 2 (a) XRD was obtained from the WO₃ film. FEG-SEM images with 50,000x magnification of (b) (A1) WO₃, (c) (A2) WO₃, (d) (B) WO₃.

Fig. 2 shows the top-view FEG-SEM images of the WO₃ (A1) film (b), the WO₃ (A2) film (c) and WO₃ (B) film (d). Where nanotubular structures present similar characteristics.