

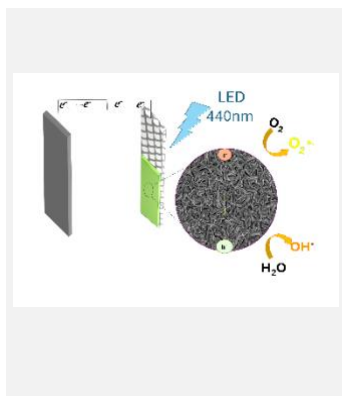
Application of WO₃ photoanodes deposited on titanium mesh for environmental remediation processes in reactors

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The development of materials with good photoelectrocatalytic properties is a current need due to the increase of recalcitrant compounds in water sources. In this work, WO₃ films were deposited on titanium meshes by a wet chemical method that aims to produce nanoplates. Different calcination temperatures (400-600 °C) were studied, with 500°C as the best temperature. The Ti-WO₃ film at 500°C presented a photocurrent density of 4.7 mA cm⁻² and degraded 88% of a 4-NP solution (C₀ = 10ppm) after 120 min in a flow reactor under 440nm LED irradiation.

Introduction

Photoelectrocatalysis is a technology involving a photocatalytic system that applies an external positive bias, which can significantly increase the rates of photocatalytic reactions by driving the photogenerated electron-shell (e^-/h^+) pairs in opposite directions and thus reducing their recombination tasks [1]. The development of a cost-effective photoelectrocatalytic reactor and its combination with anodes with improved properties play a key role in environmental remediation as well as other applications. Tungsten oxide (WO₃) is an n-type semiconductor that has different polymorphic forms; however, it has been demonstrated that the most active crystal structure for photoelectrochemical reactions is the monoclinic one. It has an indirect band gap (E_g) that can vary in a range between 2.4 and 2.8 eV depending on the synthesis process. Therefore, WO₃ absorbs in a part of the visible region of the solar spectrum (≤ 480 nm) and the UV region. In addition, this material has better electron mobility (~ 12 cm² V⁻¹ s⁻¹) compared to TiO₂ (~ 0.3 cm² V⁻¹ s⁻¹) and presents excellent stability in acidic aqueous solutions [2]. Therefore, WO₃ films were synthesized by the peroxotungstate reduction method, their properties were analyzed for different calcination temperature conditions, and the material under optimized conditions was applied for 4-nitrophenol degradation.

Material and Methods

The WO₃ was deposited on a titanium mesh

substrate (Ti-mesh) cut into 2 x 2 cm and cleaned by treatment. In the first step of the synthesis process, a layer of WO₃ film was deposited on clean Ti-mesh by reduction of peroxotungstate. Briefly, 4.84 mmol of sodium tungstate, 4.80 mmol of ammonium oxalate, and 132 mL of water were successively added to a jacketed glass reactor under magnetic stirring. After that, 36 mL of concentrated HCl, 32 mL of hydrogen peroxide (37%), and 120 mL of ethanol were added dropwise under stirring, respectively. The Ti-mesh was added to the final solution in a vertical position with the reactor wall for three hours at 85 °C for the deposition of the WO₃ film. The film was calcined for two hours at 500°C in a muffle oven with a heating rate of 1 °C min⁻¹. The calcination temperature of WO₃ in Ti-mesh also was studied at 400 and 600 °C. The materials synthesized in this study were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Linear sweep voltammetry (LSV) in 0.1 mol L⁻¹ NaCl applying 440nm LED irradiation.

Results and Discussion

Figure 1 presents the SEM, XRD, and LSV results for WO₃ films deposited on Ti substrate at 400, 500, and 600 °C (referred to as WO400, WO500, and WO600). As observed, the calcination temperature significantly influenced the morphology and characteristics of the Ti-WO₃ film obtained [3-4]. At all studied calcination temperatures, a nanoplate morphology is observed. However, the length and thickness profiles of the particles obtained for

WO400, WO500, and WO600 vary with the temperature change, as shown in the comparative graph of Fig. 1 (a-c). The WO400 film had a length and thickness of 387.56 nm and 81.30 nm, respectively. When the calcination temperature was increased to 500 °C, the length and thickness values changed, with the nanoplate length increasing to 902.0 nm and the thickness decreasing to 47.8 nm, resulting in a rougher film. Conversely, when the temperature was increased to 600 °C, a reduction in the length of the nanoplates to 564.5 nm and a thickness of 86.10 nm was observed (Fig. 1 (d-i)). The modifications in these morphological parameters were essential for understanding the qualities of the WO₃ films and the variations in the photoelectrochemical responses of the WO400, WO500, and WO600 films.

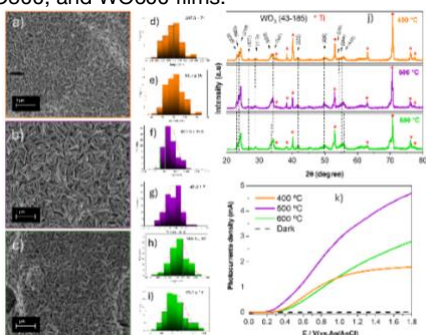


Figure 1. SEM, XRD, and LSV results for WO₃ films deposited on Ti substrate at 400, 500, and 600 °C.

The X-ray diffraction (XRD) patterns for the WO400, WO500, and WO600 films are presented in Figure 1(j). All films at different temperatures exhibit a characteristic monoclinic WO₃ structure with three prominent peaks in the 22 to 25° region, which aligns well with the JCPDS 43-1035 standard reference [4]. The increased intensities of the peaks belonging to the structure of the WO500 film may indicate an improvement in the crystallinity of this material, which is consistent with the modifications

Conclusions

The synthesized films presented photoelectrochemical responses according to their morphological and structural properties. When calcined at 500 °C, the Ti-WO₃ film presented a photocurrent density of ca. 4.7 mA cm⁻², being 2 and 3 times higher than that obtained for the films at 600 and 400 °C, respectively. The optimization conditions for the Ti-WO₃ film resulted in the degradation of 88% of 4-NP, a recalcitrant and difficult-to-eliminate compound.

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observed in the SEM results. The photocurrent results shown in Figure 1(k) were crucial to select the film under optimal conditions, as observed in the photoelectrochemical response of 0.0 to 1.8 V vs. Ag/AgCl in 0.1 mol L⁻¹ NaCl. The film calcined at 500 °C exhibited a photocurrent density of approximately 4.7 mA cm⁻², while the films calcined at 400 °C and 600 °C showed photocurrent densities of about 1.8 and 2.8 mA cm⁻², respectively. These results demonstrate that the morphological and structural modifications undergone during calcination at 500 °C favored better charge separation at the electrode and suppression of electron-hole pair (e⁻/h⁺) recombination, resulting in a higher photocurrent density.

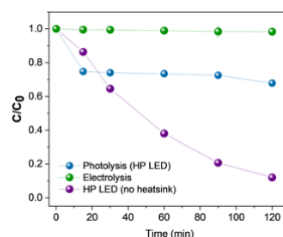


Figure 2. Degradation tests of 4-nitrophenol ($C_0 = 10$ ppm) for 120 min in NaCl 0.1 mol L⁻¹ applying 1.5 V vs. RHE by photolysis, electrolysis, and photoelectrocatalysis.

Figure 2 shows the photocatalytic response of the 500°C electrode in the degradation of 4-nitrophenol (4-NP) of initial concentration 10ppm applying 1.5V vs. RHE in a photoelectrocatalytic reactor coupled with 440nm LEDs for 120 min. As observed, photolysis and electrolysis were only able to degrade 25 and 8% of 4-NP, respectively. When applying the combination of the processes with photoelectrocatalysis, it was possible to obtain a degradation of 88% of 4-NP, a highly recalcitrant and with a difficult to degrade compound that is applied in the production of agricultural compounds.