Photoelectrochemical and photocatalytic properties of nanocrystalline TiO₂ electrodes

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ABSTRACT

The electrochemical and photocatalytic properties of a TiO₂ film deposited on transparent electrodes were investigated. Its electrochemical behavior was typical of an n-type semiconductor electrode. Its photocatalytic activity, investigated for phenol degradation on an optical bench (area of 1 cm², 5 mL of solution), revealed small currents (3 µA) and poor total organic carbon (TOC) removal (5 %) when the electrode was biased at + 1.1 V in the dark for 3 h. Under polychromatic irradiation, the electrode presented 25 µA of current and 12 % of phenol degradation. A better performance was achieved for photoelectrocatalytic configuration, when the electrode was irradiated and biased with + 0.6 V. Experiments done under irradiation with a metallic vapor lamp using 9 cm² electrodes and 10 mL of solution revealed that heterogeneous photocatalysis configuration (HPC) resulted in 50 % of TOC removal, while 85 % was achieved by the electro-assisted process (EHPC). Both the configurations exhibited pseudo-first order kinetics for phenol degradation, but the rate constant was two times that of EHPC. The application of a potential bias to the TiO₂ porous electrode must enhance the photogenerated electron/hole separation, which minimize the charge recombination and increases its photocatalytic activity towards organic pollutant degradation.

Keywords: heterogeneous photocatalysis, TiO₂ electrode, photoelectrocatalysis, phenol

1. INTRODUCTION

Heterogeneous photocatalysis using semiconductor oxides, as well as other “advanced oxidative processes” (AOP), is a promising alternative for wastewater treatment, because it promotes the degradation of toxic and refractory organic pollutants to harmless compounds. Degradation of phenols, for instance, is a matter of great interest, since these chemical pollutants persist in residual water discharged from several industries (oil refineries, petrochemicals, pharmaceuticals, textiles factories and others), and can be found in soils and groundwater.[1-3] After Fujishima and Honda [4] reported the photoinduced splitting of water over TiO₂ electrodes, semiconductor oxides have been widely investigated in heterogeneous photocatalysis for oxidative decomposition of organic pollutants. In this process, irradiation with the appropriate wavelength, promotes a charge separation in electron/hole (e⁻/h⁺) pairs at the surface of the semiconductor. Then, a series of reactions involving the positive hole or reactive species such as •OH and O₂•⁻ radicals, H₂O₂, etc, can result in the complete degradation of the pollutants.[5,6] TiO₂ presents photoactivity for UV irradiation and has been extensively studied as photocatalyst for environmental application because it is a non-toxic material that exhibits biological and chemical stability and low cost.[1] Usually, suspensions of fine TiO₂ particles are used, and the efficiency for the process is guaranteed by the large surface area of the catalyst. However, the methods for separating out the oxide particles is impractical and costly and thus hinders its industrial application.[7]

A better approach consists of using an immobilized form of the photocatalyst deposited onto an electrically conducting substrate. An application of a small anodic potential bias to the TiO₂ film increases the separation of photogenerated electrons and holes, also suppressing its recombination. Since the charge recombination is major limiting factor for heterogeneous photocatalysis, the electrochemically-assisted process can exhibit higher efficiency.[8,9] Literature reports on several studies of this strategy, developed with TiO₂ films deposited on the surface of titanium or transparent glass electrodes. In general, it was reported that photoelectrocatalytic configuration, i.e., the electrochemically-assisted process, exhibits higher efficiency for pollutant degradation than the photocatalytic one.[10-18]

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Investigation of the electrochemical and photoelectrochemical properties of the semiconductor electrodes and its influence on the photocatalytic activity has also been reported. However, the practical application of TiO₂ electrode as photocatalyst for water purification has not yet been achieved. Motivated to improve the applicability and the efficiency of TiO₂ electrodes for environmental purposes, we are investigating the electrochemical properties of nanocrystalline TiO₂ porous electrodes and its activity for oxidative decomposition of phenol by electroassisted heterogeneous photocatalysis.

2. EXPERIMENTAL DETAILS

2.1 Preparation and characterization of the porous TiO₂ electrodes

All the chemicals were of p.a. grade and used without any further purification. Deionized water from a Milli-Q water purification system was used throughout the work. Fluorine-doped tin oxide transparent conducting glass, glass-FTO (Hartford glass Co. Inc., Rₛ < 10 Ωcm) was used as substrate for the porous TiO₂ electrodes. A small aliquot of an aqueous suspension of nanocrystalline TiO₂ particles (diameter of ca. 25 nm, HPW Catalysts & Chemicals Ind. Co., Ltd.) and polyethylene glycol was spread onto the transparent electrode with a glass rod using adhesive tape as spacer, followed by heating at 450°C for 30 min. The surface of the films was examined using a JEOL JSM 63601V scanning electron microscope (SEM) with energy-dispersive X-Ray analysis (EDX). The thickness of the films was measured by profilometry (Alpha Tencor step 200).

The electrochemical properties of the glass-FTO|TiO₂ porous electrodes were investigated in aqueous solutions with Na₂SO₄ 0.1 mol L⁻¹ as supporting electrolyte. A three-electrode, single-compartment glass cell with optic glass window was used, with a Pt wire as counter-electrode. The reference electrode, Ag/AgCl (in aqueous 3 mol L⁻¹ KCl), was placed in a capillary of Luggin. Electrochemical measurements were performed with an Eco-Chimie Autolab PGSTAT-10 in the dark and under irradiation in an optical bench consisted of an Oriel Xe (Hg) lamp, water and cut-off filters and neutral density lens. Light intensity was measured with a Newport Optical Power Meter.

2.2 Photocatalytic activity of the porous TiO₂ electrodes for phenol degradation

The photocatalytic activity of the TiO₂ electrodes was investigated under irradiation on the optic bench and with a metallic vapor discharge lamp using aqueous solution containing 50 mg L⁻¹ of phenol. On the optical bench, the experiments were performed using glass-FTO|TiO₂ electrodes (geometrical area = 1.0 cm²) and 5 mL of phenol solution. The experiments were conducted using a cell configuration for electrolysis, with the working electrode facing the Pt counter-electrode. The anode was irradiated from the backside (through the FTO glass), and the variation of the current with time was accompanied during 3 hours by chronoamperometry, by application of a fixed potential value to the working electrode against the counter-electrode (potentiostatic control).

The electrochemical oxidation studies were performed in the dark (EC); heterogeneous photocatalysis (HPC) under polychromatic irradiation (and application of 0.0 V to the glass-FTO|TiO₂); and electrochemically-assisted photocatalysis (EHPC), on an irradiated and +0.6 V positively biased TiO₂ electrode. Kinetics of the phenol degradation reaction was investigated by irradiation with a metallic vapour discharge lamp, using porous electrodes with larger active area (9.0 cm²) and 10 mL of phenol solution. The amount of phenol degradation was estimated immediately after the period of irradiation, from measuring the concentration of dissolved organic carbon with a total organic carbon analyzer (TOC-5000 Shimadzu). Investigation of intermediates in the irradiated phenol solution was accomplished by high-pressure liquid chromatograph system with UV detector (Shimadzu HPLC instrument), using a mixture of acetonitrile/water/acetic acid, 68/33/4 (V/V) as mobile phase for the reversal phase column. The UV detector was set at 270 nm and the flow rate was 1.0 mL min⁻¹. The solutions were also analyzed by UV-Visible absorption spectroscopy (Hewlett-Packard UV-Vis spectrophotometer model 8453). Experiments were also performed for “blank” control (photoysis without the TiO₂ film). Duplicate experiments were carried out under each experimental condition to confirm reproducibility.

3. RESULTS AND DISCUSSION

3.1 Characterization of the TiO₂ electrodes

The TiO₂ films deposited from aqueous TiO₂ suspension on glass-FTO electrodes were transparent and mechanically stable. From profilometry, as well as from a SEM cross-section analysis of a fractured sample, the thickness of the films...
were estimated in ca. (4.0 ± 0.5) µm. SEM analysis revealed a very uniform and porous surface consisted of agglomerated small particles, as observed in Fig. 1. Also, from EDX analysis, the Ti/O ratio was approximately estimated as 1:2 from the O peak at 0.523 keV and the Ti peak at 4.51 keV. 

![SEM images of the surface of TiO$_2$ film deposited onto glass-FTO.](image)

The electrochemical properties of the TiO$_2$ electrodes in aqueous 0.1 mol L$^{-1}$ Na$_2$SO$_4$ were investigated in the dark and under polychromatic irradiation. In the dark, the open circuit potential slowly decreased, exhibiting a constant value, $V_{OC} = 0.20$ V, 15 minutes after dipping the electrode into the supporting electrolyte solution. Cyclic voltammetry revealed a wide potential window, limited at −0.2 and +1.3 V (vs Ag/AgCl) due to H$_2$ and O$_2$ evolution. Defined peaks were observed for the electron transfer reaction of ferri/ferrocyanide redox couple, as can be seen in Figure 2.

![Cyclic Voltammogram for the glass-FTO and glass-FTO/TiO$_2$ electrodes in 1x10$^{-3}$ mol L$^{-1}$ K$_4$Fe(CN)$_6$ aqueous solution (in 0.1 mol L$^{-1}$ Na$_2$SO$_4$) at 15 mV s$^{-1}$.](image)

The substrate, glass-FTO electrode, exhibited a similar behavior with slightly larger current values. Analysis of the voltammograms determined at different scan rates (ν) revealed that the peak current was a linear function of $\nu^{1/2}$ up to 20 mV s$^{-1}$. Also, the difference between the anodic and cathodic peaks was higher than the 59 mV expected value for this reaction, and enlarged with increasing scan rates, revealing that this redox system was not reversible at both the glass-
FTO and glass-FTO|TiO₂ electrodes. The cathodic peak, observed at +0.21 V, is in good agreement with the reported values obtained with SnO₂ and Pt electrodes. On the other hand, the anodic oxidation of ferrocyanide occurred at potential more anodic than the corresponding reported data. This behavior, already reported for tin oxide electrodes, is characteristic for n-type semiconductor materials in redox systems with potential higher than its flat band potential. Thus, majority charge carriers are removed from the surface (depletion layer), the charge transfer reactions making more difficult. Moreover, the lower currents observed for the porous glass-FTO|TiO₂ electrode in comparison to its substrate (glass-FTO) can be attributed to the TiO₂ film. The film must affect the transport of redox species from the bulk solution to the electrode surface (ferrocyanide/ferrocyanide diffusion) as well as, due to its resistive characteristics, reduce the charge transfer rate at the internal semiconductor/electrolyte interface. Under irradiation, the electrochemical response of the porous glass-FTO|TiO₂ electrode varied with the light intensity. The open circuit potential in supporting electrolyte, which corresponded to 0.20 V in the dark, changed to -0.15 V under 10 mW cm⁻² of polychromatic irradiation. Under 50 and 100 mW cm⁻², the Voc values corresponded respectively to -0.22 V and -0.35 V. The variation of the open circuit voltage to more negative values, which depended on the light intensity, can be attributed to the electron injection into the conduction band of TiO₂ after the e⁻/h⁺ charge separation.

3.2 Photocatalytic activity of the porous TiO₂ electrodes for phenol degradation

Figure 3 exhibits the cyclic voltammograms obtained for the glass-FTO|TiO₂ electrode in aqueous solution of 0.1 mol L⁻¹ Na₂SO₄ containing 50 mg L⁻¹ of phenol. In the absence of irradiation, the phenol solution exhibits the onset anodic current at 1.1 V (vs Ag/AgCl), near the potential for O₂ evolution reaction in the supporting electrolyte. Literature reports similar results for a RuO₂-TiO₂/Ti electrode in aqueous solution of phenol 0.01 mol L⁻¹ (in H₂SO₄ 0.5 mol L⁻¹), and the peak observed at 1.0 V was attributed to the formation of phenoxy radical, which is the first step in phenol electrooxidation. Under polychromatic irradiation (100 mW cm⁻²), larger current values were observed. As expected for a semiconductive electrode, higher photocurrent values are observed for increasing the positive applied potential, as already reported for irradiated Ti/TiO₂ electrodes in aniline aqueous solutions.

![Cyclic Voltammogram for the glass-FTO|TiO₂ electrode in aqueous solution with 50 mg L⁻¹ of phenol](http://proceedings.spiedigitallibrary.org/)

Fig. 3. Cyclic Voltammogram for the glass-FTO|TiO₂ electrode (area of 1 cm²) in aqueous solution with 50 mg L⁻¹ of phenol (in 0.1 mol L⁻¹ Na₂SO₄) obtained at 15 mV s⁻¹ in the dark and under polychromatic irradiation (100 mW cm⁻²).

Figure 4 exhibits the variation of the current generated by the porous TiO₂ electrode in phenol solution for electrochemical oxidation in the dark (EC), for heterogeneous photocatalysis under irradiation (HPC), and for electrochemically-assisted photocatalysis (EHPC). Fig. 4 revealed that, in the dark, when the glass-FTO|TiO₂ electrode is positively biased at 1.1 V, which corresponds to the onset for phenol oxidation (Fig 3), just a small current of 2 µA was observed. This treatment was applied for 3 hours and then the solution and the surface of the electrode were analyzed. Determination of TOC revealed that 5 % of the pollutant was mineralized in the solution. The surface of the electrode, which became slight brown-colored, was rinsed with water and examined by SEM. The morphology of the surface electrode was almost similar to that of the as-prepared sample, but exhibited less-defined grain boundaries. Also, EDX
analysis detected a considerable quantity of carbon at the surface (8% of the composition), which can be an indicative that an organic film deposited at the electrode surface. It was reported that the electrooxidation of phenol on different electrodes (RuO$_2$-TiO$_2$/Ti, Pt and graphite), under low current densities, resulted in deposition of a polyoxyphenylene film which inactive the electrode [28]. This is also concordant with the low current observed for EC configuration (Fig. 4) and the poor TOC removal. In the case of the heterogeneous photocatalysis (HPC), an open circuit potential of -0.6 V was observed for the irradiated porous TiO$_2$ electrode. For the HPC configuration in short-circuit conditions, with no external potential applied to the electrode, the current exhibited by the system ranged from 0.03 to 0.027 mA (Fig. 4). TOC measurements revealed 12% of phenol degradation in the solution after 3 hours of irradiation. Higher efficiency for phenol degradation was observed for photoelectrocatalysis configuration. Application of +0.6 V to the irradiated electrode resulted in higher current values than the observed in EC and HPC configurations (Fig. 4). The EHPC configuration also resulted in higher degree of TOC removal, indicating 24% of phenol mineralization. SEM images taken from the electrodes used for HPC and EHPC experiments revealed no considerable alterations in comparison to the characteristics of a freshly prepared electrode.

![Graph](image.png)

Fig. 4. Variation of the current for glass-FTO/TiO$_2$ electrodes (1 cm$^2$) in 50 mg L$^{-1}$ phenol aqueous solution (in 0.1 mol L$^{-1}$ Na$_2$SO$_4$) determined at configurations for electrochemical oxidation in the dark (EC); heterogeneous photocatalysis under irradiation (HPC); and for electrochemically-assisted photocatalysis (EHPC).

The experiments were also performed using a 400 W metallic vapour discharge lamp for porous electrodes with 9 cm$^2$ (geometrical area) in 10 mL of phenol solution. In this condition, the higher relative area/volume resulted in higher efficiency for the HPC and EHPC configurations. After 4 hours of irradiation, HPC configuration resulted in 50% of phenol degradation. The solution was also analyzed by HPLC, which identified 32% of phenol, 15% of hydroquinone and 5% of benzoquinone (intermediates for phenol photodegradation). Also, as observed for the experiments carried out using the optical bench, EHPC configuration resulted in higher degree of phenol mineralization, with 85% of TOC removal in the solution. HPLC analysis indicated that the remaining TOC at this solution can be attributed to a very small quantity of phenol (<4%), hydroquinone and benzoquinone (10% and 4%, respectively). The remaining TOC was determined as 85% for a “blank control”, i.e., a phenol solution irradiated in similar conditions without TiO$_2$ electrode, and HPLC analysis identified it as phenol (with no contribution of hydroquinone and neither benzoquinone). The UV-vis absorption spectra of these solutions were represented in Fig. 5. Compared to the freshly prepared phenol solution (prior to irradiation), the HPC irradiated sample (50% of TOC removal) presents new absorption peaks (300 to 400 nm) and a less intense absorption peak at 270 nm. Considering the residual TOC and the HPLC results, this also indicates an accumulation of intermediate organic products [28,32]. Thus, it can be concluded that the complete degradation of phenol was not achieved after 4 h of irradiation by the HPC configuration. On the other hand, a different spectrum was obtained for the EHPC irradiated solution. A low intense peak can be observed at 270 nm, in agreement with the high degree of TOC removal (85%) and the results obtained from HPLC analysis. Therefore, the porous TiO$_2$ electrode is very efficient for phenol degradation at the EHPC configuration.
Fig. 5. UV-vis spectra taken for phenol solution and for solutions irradiated using TiO$_2$ photoelectrodes in heterogeneous photocatalysis (HPC) and photoelectrocatalysis (EHPC) configuration.

Fig. 6 presents the variation of TOC reduction with time for the irradiated phenol samples (media from experiments carried out in triplicate). The data could be fitted considering first-order kinetics, then the constant rate values estimated to the HPC and EHPC configuration were, respectively, -0.22 h$^{-1}$ and -0.51 h$^{-1}$. Degradation of organic pollutants by heterogeneous photocatalysis usually exhibits pseudo-first order kinetics, depending only on the pollutant concentration, which is attributed to the high and constant concentration of hydroxyl radicals. [1]

The mechanism of phenol degradation by electrochemical and photocatalytic procedures has been extensively discussed in Literature. [3, 28-31] The oxidation process begins with formation of phenoxy radical, followed by formation of hydroquinone and benzoquinone. If oxidation proceeds for these intermediates, opening the aromatic ring, organic aliphatic acids are produced (maleic, succinic and oxalic acid). After that, oxidation of these acids produced CO$_2$ (total mineralization). [3, 28-32] The limiting steps to the complete phenol degradation are related to the aromatic ring breakage.
and maleic acid oxidation. For electrochemical processes, depending on the characteristics of anode surface towards benzoquinone oxidation, this intermediate can accumulate and react with phenoxy radicals, resulting in polymeric products. These polymeric compounds, refractory to electrochemical oxidation, can deposit at the surface, inactivating the electrode. For the photocatalytic reaction with TiO$_2$, UV irradiation promotes the charge separation in ($e^-/h^+$) pairs. Meanwhile the electron can be trapped by O$_2$, the hole can directly react with organic pollutants or generate the very reactive •OH radicals. The high concentration of reactive hydroxyl radicals on the TiO$_2$ surface, which easily attack the aromatic ring, promotes the complete phenol oxidation. The electro-assisted photocatalytic process results in higher efficiency for pollutant degradation. The potential bias applied to TiO$_2$ electrode provides a potential gradient that drives electrons and holes to opposite directions, thus enhancing the charge separation. This minimizes the charge recombination, which is the major limiting factor for the HPC process.

The results obtained in this study are in accordance with the reported pathway for photocatalytic phenol degradation using TiO$_2$ electrodes. Comparison with reported data in the literature is not straightforward, since the pollutant removal efficiency can be affected by several parameters in the experimental setup. However, interesting correspondences were found. Using Ti/TiO$_2$ nanotubes for pentachlorophenol degradation, efficiency was 82% with HPC and reached 100% in the EHPC condition. However, the photolytic decomposition process must also be considered, since 57% of pollutant degradation was verified at control experiments. Using Pt-doped TiO$_2$/Ti electrode for degradation of 2,4-dichlorophenoxyacetic acid, the EC configuration resulted in current of 2.6 µA cm$^{-2}$ and 16% of the pollutant was degraded after 5 h. The EHPC process, with 3.5 V applied to irradiated electrode, gives a current ranging from 52 to 30 µA cm$^{-2}$ and 53% of degradation. Since just 27% of the pollutant degradation was achieved from HPC, it was concluded that a synergetic effect takes place when irradiation and external potential bias are supplied to the electrode. Also, the values for the constant rate changed from 0.056 to 0.14 h$^{-1}$ for the HPC and EHPC process. Compared to other electrodes, the investigated glass-FTO/TiO$_2$ electrodes exhibited good catalytic efficiency of phenol degradation, considering the high degree for phenol degradation obtained using a low cost source of irradiation and application of low potential values.

4. CONCLUSION

The glass-FTO/TiO$_2$ electrode exhibited electrochemical behavior typical of n-type semiconductor electrodes. Investigating its photocatalytic degradation of phenol on an optical bench, the electrode presented low efficiency when used as an anode in the dark, exhibiting low current densities and poor total organic carbon removal. Under polychromatic irradiation, higher current densities and phenol degradation were achieved for the heterogeneous photocatalysis configuration. The electrode performed better in the electrochemically-assisted photocatalysis process. Application of +0.6 V to the irradiated TiO$_2$ resulted in higher current density and TOC removal, indicating a synergic effect of photocatalytic and electrochemical processes. Both the configurations exhibited a pseudo-first order kinetics for phenol degradation and rate constant was twice higher for electrochemically-assisted photocatalysis process. The application of a potential bias to the TiO$_2$ porous electrode must enhance the photogenerated electron/hole separation, which minimizes the charge recombination and increases its photocatalytic activity towards organic pollutant degradation.

Acknowledgments:

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