

Photo-assisted Electrochemical Copper Removal from Cyanide Solutions Using Porous TiO₂ Thin Film Photo-anodes

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Received: November 14, 2012; Revised: July 24, 2013

TiO₂ porous films were prepared on ITO coated glass slides by the sol-gel dip-coating method assisted with Polyethylene glycol (PEG). The films were used as photo-anodes in the photo-assisted electrolytic removal of cuprous ions in cyanide media. These were characterized by SEM, UV-Visible spectroscopy and XRD. The PEG modified films were free of cracks and developed a porous structure after heat treatment at 500 °C, due to the thermal decomposition of the structure associated PEG. It was demonstrated that the photo-assisted electrochemical reduction of copper is promoted by the use of modified TiO₂ films as photo-anodes, thanks to the greater surface area given by the PEG decomposition. However, the film thickness was found to be a critical factor in the process, to such an extent that films composed of 5 layers were completely inefficient, meaning that despite the open porosity, multilayered films acted as a barrier within the photo-electrolytic process.

Keywords: porous TiO₂ thin films, sol-gel dip-coating, polyethylene glycol (PEG), photo-assisted electrolysis, copper ion removal

1. Introduction

Titanium dioxide (TiO₂) offers an excellent chemical stability over a wide pH range and in an elevated number of solvents. Furthermore it presents a high chemical resistance under illumination (low photo-corrosion) and possesses the advantages of being non-toxic, safe, relatively abundant and, because of the high oxidizing power of the holes in its valence band, it has the capacity to completely mineralize most of the pollutants of industrial concern. All these properties make the TiO₂ the material chosen by excellence for photo-catalytic applications¹.

In recent years, an important part of the applications of the titanium dioxide has been focused on the purification and treatment of aqueous and gaseous currents contaminated by organic compounds and/or metallic ions employing particulate TiO₂²⁻¹³. Specially, the metal ions removal has received certain attention due to the feasibility of valuable metals recuperation^{7,9,12}. The metal ions present in effluents are usually found to be complexed by substances like EDTA or Cyanide, species widely employed for industrial applications. The photo-catalytic treatment of these solutions showed several problems. For example, whereas the EDTA oxidation is achieved, the metal ions reduction is not attained⁹. On the other hand, when cyanide complexes are present, normally it is required to add a hole scavenger (generally an alcohol) to enhance the metal complex reduction, inhibiting the oxidation of CN⁻, resulting in an undesirable accumulation of such toxic species in the solution⁷.

Although the results obtained with particulate materials have shown that the heterogeneous photo-catalysis is

a promising alternative for remediation of that type of effluents, they have also revealed disadvantages related with the separation, recovery and recycling of the catalyst and metallic deposits from the treated effluents^{4,5,14}. An alternative and effective methodology to overcome these inconveniences is the photo-assisted electrolysis¹¹. Here, the TiO₂ is supported on a conductive substrate to be used as anode and is coupled with a conductive material acting as a cathode. In this system, the metals ions are reduced over a metallic electrode allowing its recovery, or just making easier its disposal. Additionally, due to the imposed potential, oxidation of the complex forming agent can occur at the photo-anode, avoiding the hole scavenger addition in the solution¹⁵.

One of the most common methodologies for the elaboration of supported TiO₂ on conductive substrates is the combination of the Sol-gel process and the dip-coating or spin-coating techniques¹⁶, due to the low sintering temperatures required, versatility of the processes and homogeneity at molecular level¹⁷. However, the films obtained by this technique are generally cracked and present low surface area related to its low porosity¹⁸. Recent studies¹⁹⁻²², have pointed out the use of certain compounds called polymeric fugitive agents (PFA's) as generators of porosity, which are able to produce, after heat treatments and without obstructing the gelation, porous crack-free films that lead to photo-electrolytic activities superior to those of traditional films. Among the different PFA's employed in the literature, polyethylene glycol has some advantages such as its relatively low cost, low toxicity and molecular weight range available²³. Additionally, it has shown to provide TiO₂ with high specific surface area and roughness^{24,25}.

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In this study, a simple methodology for the preparation of TiO_2 porous thin films supported on conductive glass slides was developed, using PEG as polymeric fugitive agent. The films were characterized by X-ray diffraction, UV-Visible spectroscopy and scanning electron microscopy. Finally, the effects of PEG modification and the number of deposited layers on the photo-assisted electrolytic removal of copper in cyanide solutions were studied.

Cyanide baths are commonly employed during copper electroplating due to some advantages over other bath compositions, such as highly adherent, uniform and fine-grained deposits²³. However, waste water coming from these industries are poisonous, representing a risk for human live and the environment^{23,26-28}. There are different methodologies applied for removal the cyanide ions and recovery the copper ion in waste waters^{23,26-28}, unfortunately photo-catalysis has receive minor attention despite its advantages of being a environmentally friendly and low cost methodology²⁶. In the present study we take advantage of the photocatalysis and electrolysis to oxidize the cyanide ions and simultaneously recover the copper on a metallic substrate^{23,26}.

2. Experimental

2.1. Preparation of TiO_2 sols

The titania sols were prepared using titanium tetraisopropoxide (97%, Aldrich) as TiO_2 precursor, isopropanol (98%, Carlo Erba) as solvent, acetylacetonone (99%, Aldrich) as stabilizer, acetic acid (100%, Merck) as pH adjuster and granular polyethylene glycol (Carbowax) with molecular weight of 3350 as template agent for pore formation. The sols were prepared at room temperature, in the following order: First, 2.6 mL of acetylacetonone was added to 12.5 mL of isopropanol under constant stirring for 30 minutes. Then 5 mL of titanium tetraisopropoxide was added to the above solution and the mixture was maintained under stirring for 30 minutes. Deionized water was slowly added, drop by drop, and the solution was maintained under stirring for an extra 15 minutes. Finally, the pH was adjusted to 4 with acetic acid and polyethylene glycol was added in a concentration of 24 g/L for modified films. The sols were maintained under stirring for two hours. At this stage, the effect of the PEG addition on the stability and viscosity of the sols with time was evaluated. Such stability was evaluated in a qualitative manner, registering whether precipitates were present or not. The thermal analyses (TGA and DTG) were carried out on xerogels obtained after the desiccation of the sols at 50 °C for 24 hours. These analyses were performed at a heating rate of 5 °C/min under oxidizing atmosphere, with an air flux of 20 mL/min.

2.2. Preparation of TiO_2 photo-anodes

Glass slides covered with an Indium-Tin Oxide conductive layer (Aldrich 8-12 Ω/Sq) were used as substrates. The substrates dimensions were 25 mm \times 15 mm \times 1 mm. Before immersion, the substrates were washed with isopropanol for 30 minutes in an ultrasonic bath and were dried at room temperature under an air flux. TiO_2 layers were deposited by immersion-extraction (dip-coating) on

the corresponding sol at 10 cm/min. After deposition, the films were dried at room temperature in a dessicator for three hours and were heat treated at 500 °C for one hour with a heating rate of 5 °C/min. The process was cyclically repeated for each deposited layer. The number of deposited layers in each sample varied from 1 to 5 layers and, for the purpose of this study, the samples with 1, 3 and 5 layers were chosen for analysis.

The effects of the PEG addition and of the number of deposited layers on the optical, crystalline and morphologic properties were evaluated by means of the following techniques: UV-Visible spectroscopy in the 200-800 nm range, X-Ray diffraction using $\text{CuK}\alpha$ radiation operating at 40 kV and 40 mA, and Scanning electron microscopy operating between 5 and 15 kV.

2.3. Photo-assisted electrolytic reduction of cuprous ion in cyanide solutions

The photo-electrolytic reactor used in this study (Figure 1) consisted of a prismatic compartment with a squared base and a capacity of 50 mL of solution. The photo-anode was placed in one side of the reactor in order to illuminate the TiO_2 /electrolyte interface through a window, employing a high pressure mercury lamp (General Electric, Kolorlux, 125 W), placed at 2 cm from the photo-anode surface. In addition to 365 nm as its main line spectrum, other line spectra emitted are: 254 nm, 313 nm, 405 nm, 436 nm, 546 nm and 579 nm. The cathode was placed inside the solution and was separated from the photo-anode by a distance of 2.5 cm. It consisted of a steel sheet (AISI SAE 1020) of 40 mm \times 20 mm \times 1 mm. For all experiments the voltage between electrodes, applied by a power source, was 2.5 V. The reaction volume for all experiments was 50 mL of an 1800 ppm solution of Cu^{+1} at pH 10 and with a CN^- : Cu^{+1} molar ratio of 3:1. Such concentrations and pH values are commonly found in the wastewaters of industrial electroplating processes. The

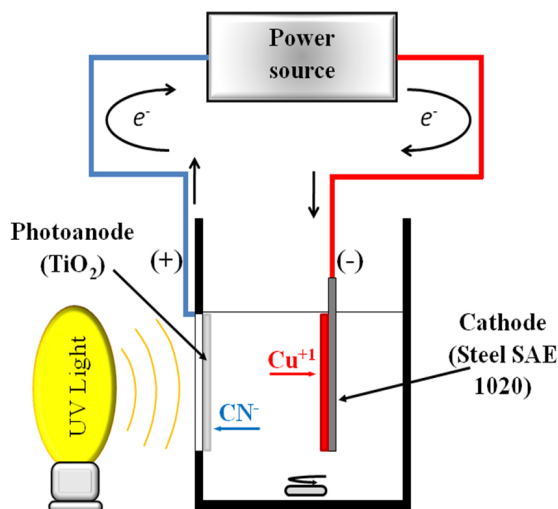


Figure 1. Schematic representation of the cell employed for photo-assisted Copper ions removal.

solution was stirred during all the reaction period (2 hours) to promote the homogeneity of the reaction volume. Before the tests, the solution was kept at dark for 15 minutes in order to smooth the humectation progress of the photo-anode. The copper concentration was followed by atomic absorption spectroscopy on samples taken along the reaction time.

3. Results and Discussion

3.1. Polyethylene glycol effect on the viscosity and stability of the TiO₂ sols

The variation of the sols viscosity with time (with and without PEG) is presented in Figure 2. There is a slight but constant increase of the viscosity of the sols with time. This behavior is a response to the progress of the hydrolysis and condensation reactions that take place inside the sol²⁹. Normally, during the aging of the sol a sharp increase on the viscosity is observed, but in this case the presence of acetylacetonate diminishes the velocity of the gelation reactions^{30,31}, which is reflected on the smooth increase of viscosity. The PEG addition also generates an increase of 0.84 cP on the initial viscosity of the sol, as a result of the thickening properties of the polymer³². The presence of PEG did not affect the stability of the sol, as they remained translucent and without displaying precipitates, which is an important factor for achieving transparent TiO₂ films.

3.2. Thermal analysis of the Xerogels obtained from the TiO₂ sols

The Xerogels thermogravimetric analysis, recorded up to 600 °C, is presented on Figure 3a. The PEG modified TiO₂ xerogel underwent a bigger weight loss than the unmodified xerogel, with values of 54.4% and 44.7% for the samples with and without PEG respectively. In both cases the biggest weight loss occurred up to 400 °C approximately, which allows to conclude that under this temperature the decomposition of the organic products was produced.

The differential thermograms (see Figure 3b) show a peak between 30 °C and 100 °C, caused by desorption of water. A pronounced peak is observed between 200 °C

and 300 °C for the PEG system and, between 300 °C and 400 °C for the system without PEG. These peaks correspond to pronounced weight losses; hence they are attributed to the organic components combustion such as the solvent, stabilizer, alcoxide and the PEG³³. The PEG modified xerogel showed a small peak between 450° and 500 °C, related to residual organic compounds within the sample.

3.3. TiO₂ films characterization

Figure 4 shows the SEM images for films with 1 and 5 layers prepared with and without PEG. The TiO₂ films without PEG present a plane and cracked morphology, as product of their contraction during heat treatment; this cracking increases with the number of layers or the thickness of the coating. On the other hand, the films prepared in the presence of PEG are free of cracks, and due to the polymer decomposition during heat treatment (between 200 and 300 °C), developed a porous structure. The perceptible cracks for the 5 layered film (Figure 4d) are really pores interconnections that grow in quantity and size with the increase in the number of layers.

XRD analyses for the 5 layered TiO₂ films with and without PEG are presented in Figure 5. As for all thin films, the peaks are not very intense because of the low quantity of material deposited and the size of the crystallites³³. For the diffractograms of both films, the most representative peak is situated in the region of 25° and corresponds to the (101) plane of the anatase, typically found for films treated at 500 °C³⁴. The diffractogram of the PEG modified film shows

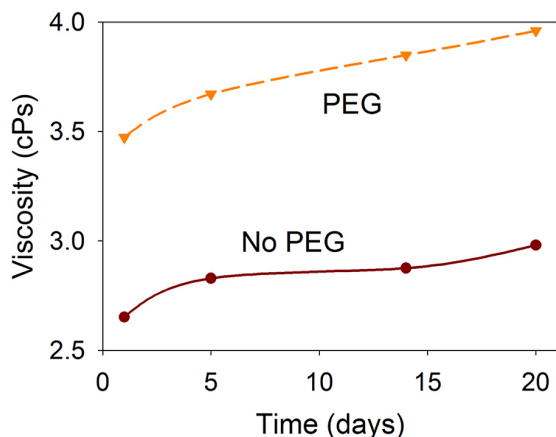


Figure 2. Viscosity vs. Time for the TiO₂ sols with and without PEG.

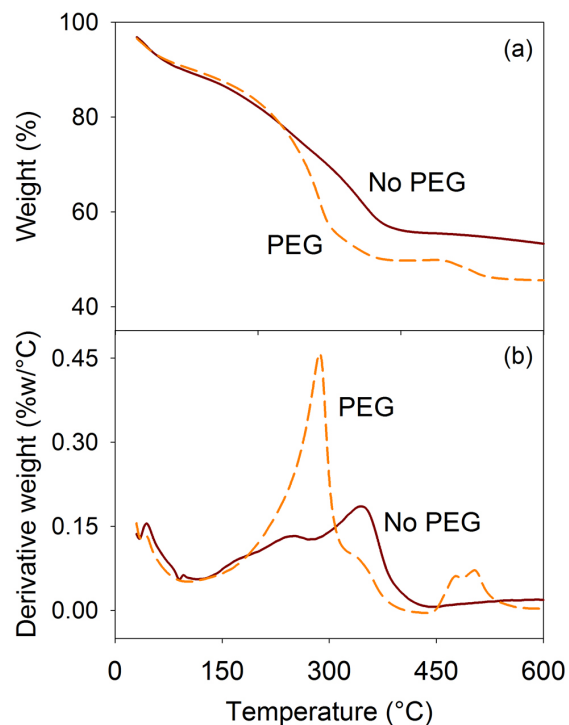


Figure 3. (a) Thermogravimetric analysis (TGA) of the xerogels, with and without PEG. (b) Differential thermogravimetry (DTG) of the xerogels, with and without PEG.

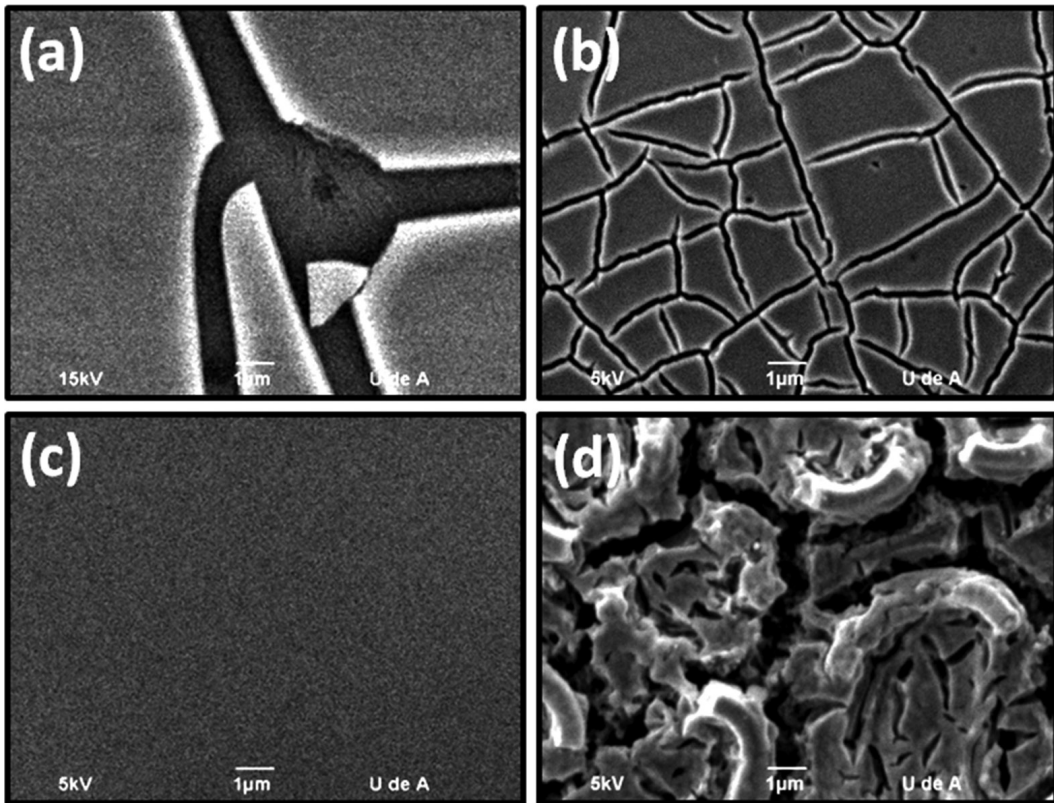


Figure 4. SEM images of the surface of the TiO_2 photo-anodes with 1 (a) and 5 (b) layers without PEG, and 1 (c) and 5 (d) layers with PEG.

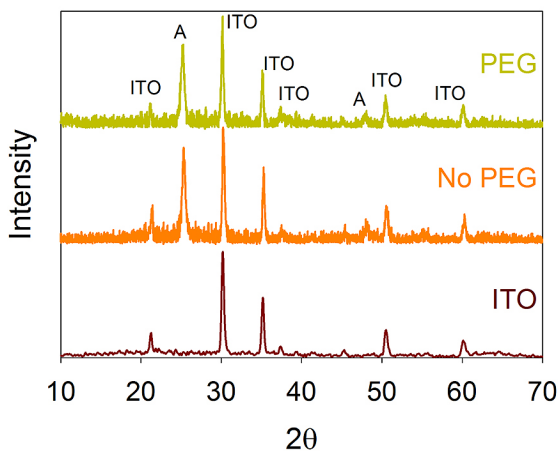


Figure 5. Diffractograms for the Substrate (ITO glass) and for the 5 layered TiO_2 films heat treated at 500°C . Letter A indicates the peaks related to the Anatase Crystalline form.

the same peaks of the unmodified film, and the intensity is also similar, which is an evidence that the polyethylene glycol does not intervene in the crystallization process at the temperature selected for heat treatment, as reported by other authors¹⁹. Additionally, employing the Scherrer equation to estimate the crystallite size of the TiO_2 in the films^{11,35}, considerable differences were not found by adding PEG as modifying agent: 17.9 ± 2.0 nm and 13.2 ± 1.2 nm for

TiO_2 films without and with PEG respectively. Confirming that PEG is only affecting the surface area of the film (see Figure 4).

Figure 6 presents the UV-Visible spectra for films with 1, 3 and 5 layers with and without modification with PEG supported on ITO glass slides. In all cases, a strong UV absorption band is observed between 300 and 400 nm, characteristic for the TiO_2 ³⁶. The same behavior of the films with the number of layers is observed in both types of films. As the number of layers increases, the film becomes less transparent due to the increase of deposited material, what translates into greater absorption intensities of the films within the UV region.

The band-gap energies of the TiO_2 films were estimated from their UV-Vis spectra (see Figure 6). The red-shift of the absorption edge of the TiO_2 films produced by the increase in the number of layers involves a decrease of the band-gap energies (E_g) from 3.55 eV (1 layer) to 3.32 eV (5 layers) for unmodified TiO_2 films and from 3.60 eV (1 layer) to 3.41 eV (5 layers) for films modified with PEG. However, due to the small shift observed in the band-gap energies, it can be assumed that the use of PEG to obtain porous TiO_2 films, does not modify the TiO_2 electronic structure, or induces states inside the band-gap of the semiconductor.

3.4. Photo-assisted electrolytic removal of copper

3.4.1. Effect of the PEG and illumination

Figure 7 shows the effect of illumination on the electrolytic removal of copper, using the 1 layered TiO_2

films. It is observed that when the unmodified TiO₂ film is employed as anode in the electrolysis, the copper removal is negligible (0.2%). However, when the TiO₂ film is irradiated with UV light, reduction of cuprous ion increases considerably, reaching 15% of metal removal in solution after 2 hours; this response shows that under illumination, the generation of e^-h^+ pairs on the TiO₂ films promotes the redox reactions taking place on the electrolysis cell.

From Figure 7 it is also evident that modification of the TiO₂ photo-anode, using PEG, favors the copper electrolysis

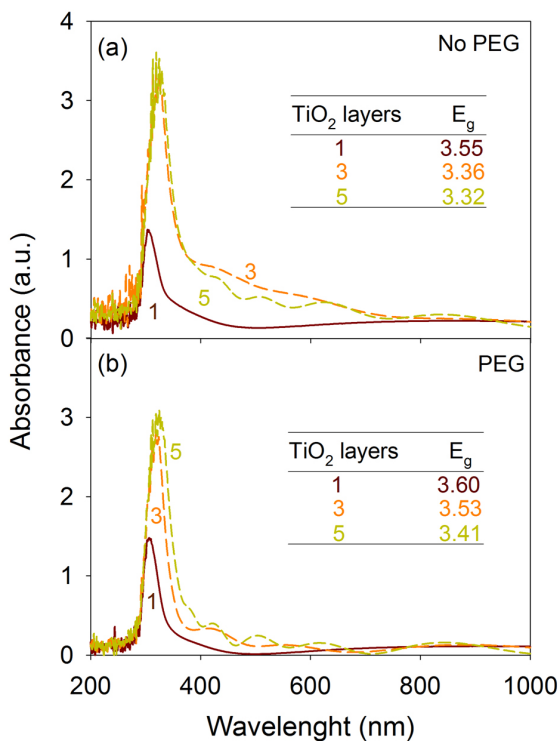


Figure 6. UV-Vis absorption spectra for the TiO₂ films with different number of layers: (a) no PEG, (b) with PEG. The E_g values estimated for the TiO₂ films are indicated in each figure.

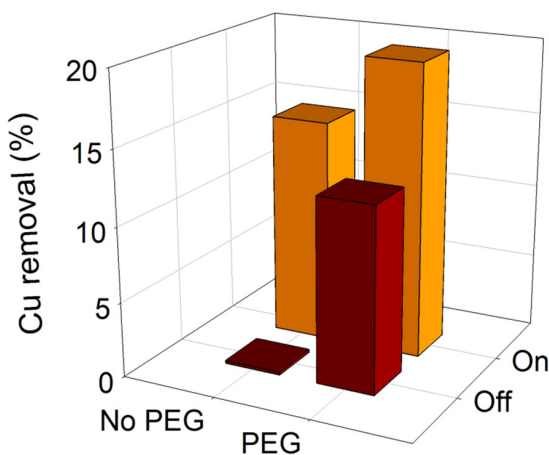
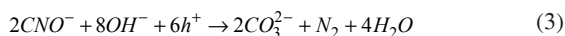
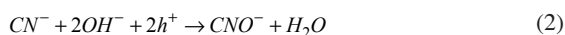


Figure 7. Copper removal for the 1 layered TiO₂ films without and under illumination.

and photo-assisted electrolysis processes, going from 0.2% (no PEG) to 12% (with PEG) of copper removal for the electrolysis and from 15% (no PEG) to 20% (with PEG) for the photo-assisted electrolysis. This effect is related to the porosity generated in the TiO₂ films by the PEG as showed in Figures 4c, d.

The greater photo-anode's porosity implies a greater surface area, hence, a greater number of active sites where anodic reactions occur. The anodic reactions implied in the process are the following³⁷:



The OH⁻ and CN⁻ ions present in solution take rapidly the h^+ from the TiO₂, diminishing in this way their recombination with the photo-generated electrons; these electrons diffuse through the TiO₂ film until they arrive to the conductive substrate, where they are transported by the external electric circuit to the cathode. On this electrode, the photo-generated electrons (Reaction (1)) catalyze the copper complexes reduction reactions, especially the reduction of Cu(CN)₃²⁻ which is the most abundant for the Cu¹-CN⁻ system according to the speciation diagrams (figure not showed here)^{37,38}, as well as the formation of hydrogen as additional reaction:



The extent of the electrolytic and photo-assisted electrolytic removal of copper is related with the current generated in the process. The differences in the current behavior for each of the tests are presented in Figure 8. The higher initial currents (4.5 and 4.7 mA) correspond to the electrolysis and photo-assisted electrolysis tests with PEG modified TiO₂ photo-anodes, which relates to their higher surface area. Additionally, the higher currents after two hours of reaction (7.3 mA) correspond to the photo-assisted electrolysis tests, caused by the catalytic effect of the UV radiation (photo-generated current), independently of the modification of the photo-anode with PEG.

An additional phenomenon is presented in curves showed in Figure 8, in which an increase and following decrease on the measured current is observed with time during the electrolysis (only for TiO₂ modified with PEG) and photo-assisted electrolysis.

A similar behavior has been reported for photo-catalytic gold recovery from cyanide solutions, where a delay time is necessary to initiate the reduction with the metal ion on the TiO₂. In this case, the improvement in the reduction rate

of gold was attributed to an enhancement in the separation of the photo-generated electron-hole pairs, induced by the presence of gold clusters on the semiconductor surface. Nevertheless, in our case, the reduction of copper is expected to occur in the cathode and no or negligible reduction of copper is expected at the TiO_2 surface.

On the other hand, this behavior can be attributed to the formation of a thin film of Cu on the cathode during the early stages of electrolysis, which facilitates the electronic transfer, causing the observed increase in current observed in Figure 8³⁹. The absent of the current increase for the current transient of unmodified TiO_2 film in the dark, Figure 8, shows that there is no considerably copper removal, and light is necessary in order to carry the cyanide oxidation and copper reduction in a measurable extension, agreeing with the results in Figure 7 and the formation of a current maximum in the Figure 8. In contrast, for TiO_2 films modified with PEG the current increase is observed during electrolytic copper removal (Figure 8), due to the enlargement of TiO_2 films surface area (Figure 4). The increment of the anode's surface area carries with it an increase of the electron flow from the anode to the cathode, which yields a higher electric charge transference (greater area under the I vs. Time curve) and hence, a higher copper removal. Additionally, when the TiO_2 film modified with PEG is illuminated, higher currents are observed together with a decrease in the time necessary to reach a maximum in the current, indicating that in these films a synergistic effect between surface and light is taking place to increase the copper removal (Figure 7).

3.4.2. Monitoring of photo-assisted electrolytic reduction of copper

The evolution of the Cu^+ concentration in solution and current with time is presented in Figure 9. The copper removal velocity diminishes at low concentration values as deduced from the slope of the concentration curve. The concentration profile during the process can be represented as an exponential function⁴⁰:

$$C = C_0 \exp(-kt) \quad (8)$$

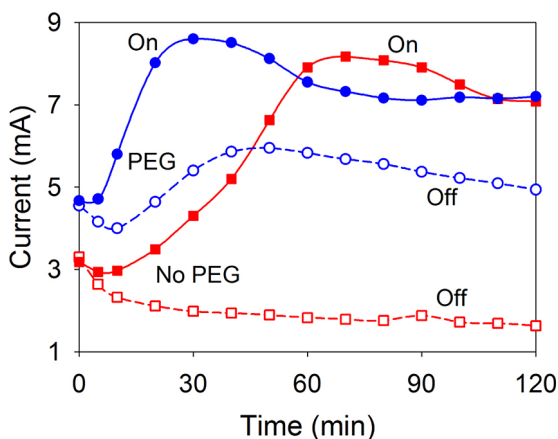


Figure 8. Current vs. Time curve for copper reduction: Electrolysis with TiO_2 films without (\square) and with PEG (\circ) and photo-assisted electrolysis without (\blacksquare) and with PEG (\bullet).

Hence, the photo-assisted electrolytic removal of copper is a pseudo-first order reaction and the kinetics can be expressed as:

$$\ln \frac{C}{C_0} = -kt \quad (9)$$

Figure 10 presents the $\ln(C/C_0)$ vs. Time curve obtained by linear regression, with $R^2 = 0.994$. The slope of the line, equivalent to the kinetic constant (k) is equal to $2.1 \times 10^{-3} \text{ min}^{-1}$. This value is among the common range of the photo-catalytic reactions⁴¹. This behavior matches the current evolution with time, presenting high values at short times (with a maximum current of 8.15 mA) and decreasing continuously with time. In spite of this kinetic behavior (diffusion control of reagent and products in the interface), the photo-assisted electrolytic removal of copper reached 63% after 8 hours.

3.4.3. Effect of the number of TiO_2 layers on the photo-anode in the photo-assisted electrolytic removal of copper

Contrary to the normally reported in the photo-catalytic tests^{13,42}, the photo-assisted electrolysis is not favored by the

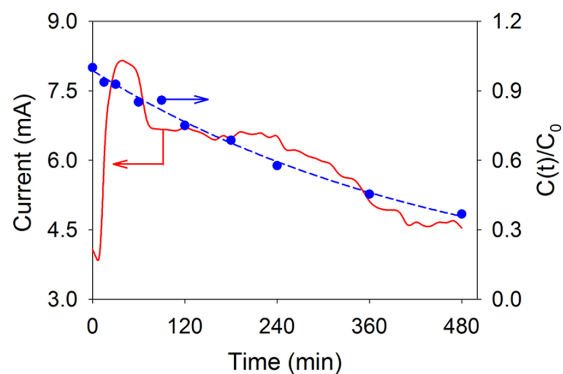


Figure 9. Copper concentration and measured current for 8 hours of reaction. The photo-assisted electrolysis was carried out with a 1 layered PEG modified TiO_2 photo-anode.

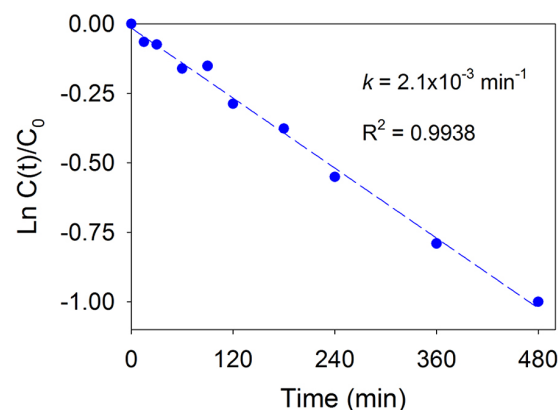


Figure 10. $\ln(C/C_0)$ vs. Time (\bullet) experimental data, and (---) linear fit. The kinetic constant was derived from the slope of the linear fit to the experimental data. 9.

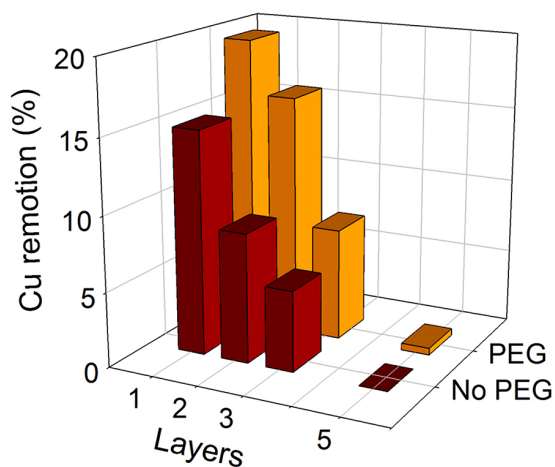


Figure 11. Copper photo-electrolytic removal for TiO₂ photo-anodes versus number of deposited layers for unmodified and modified films.

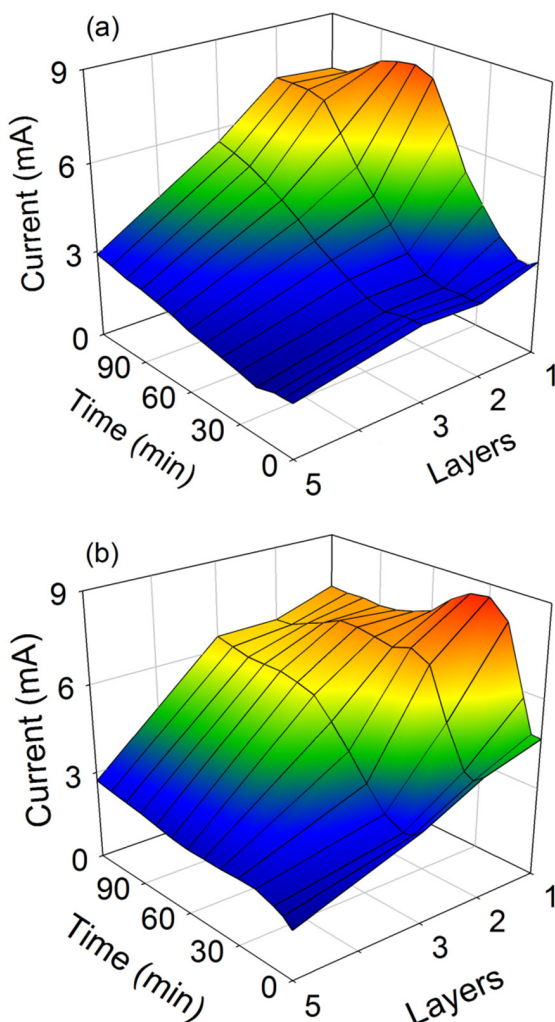


Figure 12. Current vs. Time for TiO₂ photo-anodes versus number of deposited layers for: (a) unmodified and (b) modified films.

increase in the number of layers on the film (Figure 11). Conversely, such increase in film thickness causes a detriment in the copper removal, the latter being practically negligible for films with 5 deposited layers. This behavior is noticed for PEG modified TiO₂ as for the unmodified TiO₂.

The explanation of the results in Figure 11 can be deduced from current transient presented in Figure 12. It can be observed that for both, the modified and unmodified TiO₂ photo-anodes, the electrical current drops with the increase of deposited layers reaching very low values for the films with 5 layers which correlates to the negligible copper removal for these films (Figure 11). As the number of layers increases, the potential drop throughout the film also increases, and the imposed potential (2.5 V) is not enough to accomplish the copper reduction. This phenomenon is also associated to the charge carrier recombination increase with the thickening of the film, as has been proposed by researchers⁴³⁻⁴⁷. Porous TiO₂ films are made of interconnected nanoparticles that are too small to support a space charge layer inside of them, making the diffusion of e^- through the film the only way to transport the photo-generated charge carriers. When the TiO₂ film is biased, an internal potential distribution can be presented, whose extension depends on the film thickness and the imposed potential magnitude. This electric field acts as a sink for photo-generated electrons, favoring its transport towards rear contact. In thin films, the potential distribution can be presented within the whole film, allowing the charge carriers separation that causes an increase in the currents and copper removal values. On the other hand, when the thickness of TiO₂ films is increased, the potential distribution inside the film is only presented in a small zone and near to the ITO substrate, so the recombination inside the film is increased, causing a detriment in his performance as photo-anode. Additionally to the recombination process inside the film, in the solution are also present oxidizing species (like oxygen and $\text{Cu}(\text{CN})_3^{2-}$) that can perform as electron scavengers, especially in the outermost part of the films, where the imposed potential is not high enough to favor the electron diffusion towards the ITO substrate.

The former results allow us to propose that the photo-electrolytic removal of copper using porous TiO₂ films as photo-anodes is also controlled by the electric charge transport, especially for multilayered thick films. However, further efforts to comprehend and optimize this type of cells are still needed.

4. Conclusions

The PEG has proved to be an adequate polymeric fugitive agent for the generation of porous TiO₂ thin films by the sol-gel process. The modification of the TiO₂ sol with PEG not only enables the formation of a highly porous structure, but also prevents the appearance of cracks on the films during heat treatment.

The electrolytic and photo-assisted electrolytic copper removal processes are favored by the use of porous TiO₂ thin films as anodes or photo-anodes respectively. This influence is related to enlargement in the surface area given by the open porosity generated by the PEG. Nevertheless,

despite that the increase of TiO₂ layers on the films might induce a higher surface area, these films acted as barriers for electron transport, causing a detriment on the efficiency of the process. Consequently, the copper removal is practically absent for films with 5 deposited layers.

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