Photoelectrocatalytic Wastewater Treatment Using TiO_2=ITO Bilayers Prepared on Optical Fibers by Pulsed Laser Deposition

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Abstract: Advanced oxidation processes (AOPs), on the basis of photoelectrochemical reactions, constitute a good alternative for treating wastewaters contaminated with refractory organic compounds such as dyes. For this purpose, different approaches have been explored to develop novel photoanodes that can be efficiently used in these systems. In this context, this study deals with a comparison of indium tin oxide (ITO) thin films deposited at room temperature by pulsed laser deposition on flat glass and on silica optical fiber (SiO_2 core, 600 μm diameter) substrates. Characterization data reveal that nanostructured ITO thin films with resistivity values from 4.4×10^{-2} to 5.6×10^{-4} Ω·cm were obtained. To build the photoanode, the ITO thin films were coated with a TiO_2 layer deposited by using the electrophoretic method. The prepared TiO_2/ITO bilayers on optical fibers showed a better photocatalytic performance than those deposited on flat glass substrates according to TOC and color removal measurements from dye contaminated water samples. These results suggest that the deposited materials exhibit suitable properties for their application in photoelectrocatalytic devices that, employing optical fiber as support and light transmitter, can be efficiently used for the elimination of organic contaminants in industrial wastewaters. **DOI: 10.1061/(ASCE)EE.1943-7870.0000340.**

CE Database subject headings: Fiber optics; Oxidation; Wastewater management; Lasers.

Author keywords: PLD; ITO; Optical fiber; Photoanode; Advanced oxidation processes; Wastewater treatment.

Introduction

Wastewater from various organic chemical industries has become a major environmental problem in recent decades. For example, wastewaters from textile-manufacturing industries may contain strong colored compounds, suspended particles, high hydrogen ion concentration (pH), and high chemical oxygen demand (COD). In developed countries, these wastewaters are usually treated by traditional methods that include biological, physical, and chemical approaches. In some developing countries on the other hand, these wastewaters are discharged without treatment into rivers or other natural water streams, causing serious pollution problems such as the inhibition of photosynthesis processes in water bodies and toxicity to aquatic organisms and humans (Mollah et al. 2004).

Among the remediation techniques employed to solve this environmental problem (chemical flocculation, electrofiltration, and membrane filtration), advanced oxidation processes (AOPs) have been used to increase the biodegradability of raw dye-containing wastewaters before biological treatment. These processes are chemical, photochemical, photocatalytic, or electrochemical methods characterized by the generation of the hydroxyl radical species ($OH^{\bullet}$), a chemical agent capable of oxidating almost any toxic organic compound (TOC) in wastewater (Johnson et al. 2000; Zhang et al. 2003).

Photocatalysis, which combines a semiconductor (TiO_2 or ZnO) and UV light, is one of the most promising AOPs. Owing to its high efficiency, photochemical properties, and nontoxic nature, heterogeneous photocatalysis using TiO_2 as a photocatalyst is of great interest. It has proven very effective for photocatalytic degradation of toxic and recalcitrant pollutants such as detergents, dyes, pesticides, herbicides, and other pollutants. However, problems of TiO_2 separation and reclamation need to be solved when used in an aqueous suspension and consequently, any process that avoids the filtration step would be of great practical benefit (Vinodgopal et al. 1993, Li et al. 2000).

In a previous report, the authors showed that glass optical fibers can be modified with TiO_2 to build photoanodes for photoelectrochemical wastewater reactors (Esquivel et al. 2009). The idea

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Note. This manuscript was submitted on January 8, 2010; approved on November 23, 2010; published online on November 24, 2010. Discussion period open until October 1, 2011; separate discussions must be submitted for individual papers. This paper is part of the ***Journal of Environmental Engineering***, Vol. 137, No. 5, May 1, 2011. ©ASCE, ISSN 0733-9372/2011/5-0–0/$25.00.

consisted of using a chemically treated optical fiber as both (1) the substrate for the electrophoretic deposition of a photoelectrochemically active layer of TiO_2 and (2) as a light guide inside the photoelectrochemical reactor.

During the development of this approach, we observed that the conductive layer anchored on the modified optic fiber surface (SnO_2 : Sb deposited by the painting technique) was not stable after ~5 hours of continuous use, causing electrical disconnection of the photoanode. To obtain a stable and long-lasting electrical contact along the optical fiber, a carbon thread was positioned around the optical fiber. By using this arrangement, it was possible to obtain a more controlled TiO_2 electrophoresis deposit and an electrical contact along the whole surface of the electrode (Esquivel et al. 2009). To substitute the use of the carbon thread (and reduce costs), and to have a more homogeneous deposit of the TiO_2 layer, an efficient technique to obtain a smooth, transparent, mechanically, and electrochemically stable conductive film of a suitable material that could be deposited on a cylindrical optical fiber surface had to be found.

In this context, indium tin oxide (ITO) was found to be the most widely employed compound for this purpose. In the form of a thin film deposited on glass substrates, ITO works as a transparent and conducting electrode for a wide range of applications such as solar cells, heat-reflecting mirrors, antireflective coatings, sensors, and flat panel displays (Yong et al. 2007, 2008; Moore et al. 2006; Kaneko 1987; Kim et al. 2000). ITO is a highly degenerated n-type semiconductor with a low electrical resistivity, ranging from 2×10^{-4} to 4×10^{-4} Ω·cm, a carrier concentration of approximately $10^{20} - 10^{21}$ cm^{-3}, and a wide band gap that falls between 3.3 and 4.3 eV (Viespe et al. 2007).

ITO thin films are prepared on flat surfaces (Khodorov et al. 2007) by several deposition techniques such as thermal evaporation (Prem et al. 1980; Agnihotry et al. 1985); sputtering (Kulkarni et al. 1999; Chiou and Tsai 1999); chemical vapor deposition (CVD) (Elangovan and Ramamurthi 2003); and pulsed laser deposition (PLD) (Choi et al. 2003; Ngaffo et al. 2003; Guido et al. 2004). In comparison with other techniques, PLD provides several advantages: (1) the composition of the films is quite close to that of the target, and (2) films can crystallize at low substrate temperature owing to the high kinetic energy of the chemical species in the laser-produced plasma (Kim et al. 2006). In addition, it is possible to control the size, distribution, and shape of the nanocrystals by varying deposition parameters such as target-substrate distance, laser fluence, and background gas (reactive or inert) pressure (Beena et al. 2007; Rogozin et al. 2006).

Therefore, in this work, results on the characterization and electrochemical performance of ITO thin films deposited on optical fiber and, as reference, on flat glass surfaces by laser ablation are presented. The photoelectrocatalytic properties of TiO_2 supported on the ITO films on both substrates were then evaluated in terms of the degradation (color removal and total organic carbon (TOC)) of aqueous solutions of azoic dye Orange II. Orange II belongs to a class of organic compounds known as azo dyes, which are widely used in the textile industry for dyeing. These compounds are resistant to degradation by light and oxygen and to some common acids and bases (López et al. 2004; Martínez-Huitle and Brillas 2009).

The aim of this work is therefore to show that the prepared material (ITO deposited via PLD) is useful as conductive and stable layer for the preparation of a functional TiO_2 photoanode that can be employed for wastewater treatment by using electrochemical advanced oxidation processes (EAOPs).

Materials and Methods

ITO Plasma Laser Deposition and Characterization

Laser ablation was performed by using a Q-switched Nd:YAG laser using the second harmonic line ($\lambda = 532$ nm) with a 5 ns pulse duration. The energy density (fluence) delivered to the target was approximately 3.4 J/cm^2. The laser beam focused onto a rotating high purity indium oxide-tin oxide (90–10%) target (Lesker Co). The vacuum chamber was evacuated to a base pressure of 1×10^{-5} Torr. All the experiments reported in this work were performed in an argon-oxygen atmosphere (80/20) keeping the working pressure at 1×10^{-2} Torr (Fig. 1). Thin films were deposited on flat glass and cylindrical silica optical fiber (Ocean Optics, P600-12-UV/VIS, 600 μm diameter pretreated with HF) substrates, previously cleaned in a methanol ultrasonic bath. The distance between the substrate and target was set at 5 cm. The deposits obtained were characterized as follows: X-ray diffraction (XRD) patterns were obtained by using a Bruker-AXS D8 advanced diffractometer equipped with a Cu tube to generate Cu K_α radiation ($\lambda^* = 1.5406$ Å). Raman spectra were recorded with a high-resolution micro-Raman system (LabRamHR800) by using the 632 nm line of a He-Ne laser in the backscattering configuration. Optical properties of the films (absorption coefficient, refractive index, optical band gap, and thickness) were determined from UV-Vis measurements (Agilent Technologies Spectrophotometer). Resistivity was determined from electrical resistance measurements carried out by using a 4-point probe head with a radius tip of 100 μm, spaced 1 mm (Jandel Scientific), and by electrochemical impedance spectroscopy (EIS) by using an Autolab potentiostat/galvanostat (model PGSTAT30). While the surface morphology of the deposits was evaluated by scanning electron microscopy (JEOL JSM-5400L SEM), the elements in the film were determined by energy dispersive X-ray spectroscopy (EDS). The electrochemical characterization of the films was performed in a 40 mL cell containing a sulfate buffer (0.05 M, pH 3) solution in which the thin films were incorporated as working electrode, a graphite bar as a counterelectrode and Hg/Hg_2SO_4 electrode as reference. All the experiments were performed under a nitrogen atmosphere at 298 K.

TiO_2=ITO *Bilayer Construction*

To prepare the photoanode, the ITO thin film was coated with a TiO_2 layer deposited by the electrophoretic method (Manriquez and Godínez 2007). In this manner, 50 mL of a colloidal suspension (5 g P 25 Degussa TiO_2 powder in 5% v/v 2-propanol, J.T. Baker 99.97% in deionized water) were positioned between a stainless steel sheet and the ITO coated material (the flat glass or the cylindrical optical fiber). A 4 V potential difference was applied for 60 s. Afterward, the TiO_2/ITO bilayers were sintered in an oven at 450° C (Manriquez and Godínez 2007). The geometric area of both surfaces (glass and optical fiber) was approximately the same, 1 cm^2 (five optical fibers of 4 cm length).

Orange-II Dye Oxidation Process

To test the effectiveness of the photoanode in the removal of color and TOC from a wastewater contaminated with dyes, electrocatalytic and photoelectrocatalytic experiments were carried out by using a sulfate buffer and 15 mgL^{-1} of $C_{16}H_{11}N_2NaO_4S$ (Orange II dye ALDRICH) aqueous solution. In these tests, a carbon cloth was used as the working electrode, the TiO_2/ITO bilayer as the counter and Hg/Hg_2SO_4 as the reference electrode. In this case, the experiments were performed under an oxygen atmosphere to promote oxygen reduction via two electrons at the cathode [Eq. (1)] and

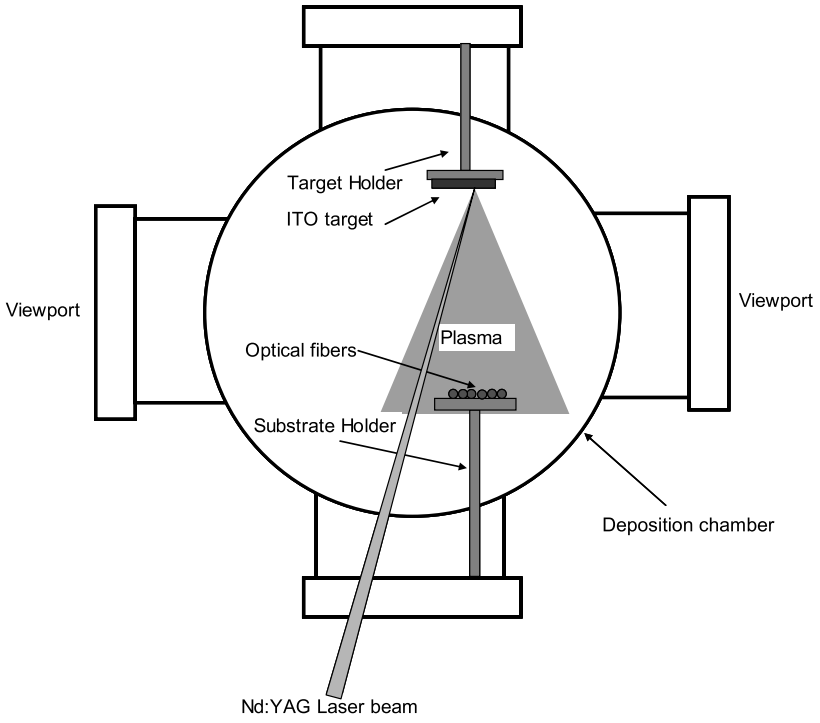


Fig. 1. Schematic diagram of the pulsed laser deposition system

the photoelectrochemical oxidation of water at the TiO_2 film [Eqs. (2)–(4)]. The presence of the hydroxyl radical ($OH^{\bullet}$) at the TiO_2/ITO photoelectrode favors a high oxidating environment (Peralta-Hernández et al. 2007; Danion et al. 2004; Zhang et al. 2008)

$$O_{2(g)} + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb} \quad (2)$$

$$h^+_{vb} + H_2O \rightarrow OH^{\bullet} + H^+ \quad (3)$$

$$h^+_{vb} + OH^- \rightarrow OH^{\bullet} \quad (4)$$

The experiments were performed under galvanostatic conditions, by applying 1 $mAcm^{-2}$ cathodic current density by using a VoltaLab potentiostat/galvanostat (PGZ 301). For the photoassisted process the system was illuminated by using a low-pressure mercury lamp ($\lambda = 254$ nm, at a power density of 21 Wcm^{-2}). For TOC analysis, a TOC-V_{CSN} analyzer (Shimadzu Co.) was employed (Esquivel et al. 2009).

Results and Discussion

ITO deposits on two groups of samples were prepared for the proposed study. The first group was prepared on pieces of flat glass, and the deposit allowed for determining the growing conditions, structural and electrochemical characterization, resistivity measurements, and the optical properties of the material. The second group was prepared on optical fibers modified under the same deposition conditions so that it was possible to compare resistivity measurements and the electrochemical characterization data with that of the flat surface. In this way, it was possible to study the performance of both types of substrate geometries for photoanode applications in EAOPs for wastewater treatment.

Structural Characterization

Fig. 2 shows the Raman spectra of the ITO films prepared by annealing at different temperatures (flat surface). To the best of the authors' knowledge, the Raman features of ITO films have not been reported and little information on the Raman frequencies of In_2O_3 is available. However, assuming that ITO films retain the crystal structure of bulk undoped In_2O_3, the Raman spectrum of ITO should be very similar to that of In_2O_3. In this manner, Fig. 2 shows three spectra corresponding to the as deposited film [Fig. 2(a)], the film annealed at 200°C [Fig. 2(b)] and at 400°C [Fig. 2(c)]. The Raman spectrum in Fig. 2(a) consists of a broad peak at 538 cm^{-1}, suggesting the formation of a nanostructured material. As the annealing temperature is increased, new features appear in the Raman spectra, in good agreement with the spectrum of In_2O_3 (Aswal and Gupta 2006) (see Table 1) and at 400°C well-defined peaks at 105, 125, 301, 367, 491, and 625 cm^{-1} can be observed.

To obtain a better understanding of what is happening with the ITO film, Raman spectra 2a and 2b were fitted by using Gaussian functions. The fitted peaks are shown in Figs. 2(a) and 2(b), and their positions are presented in Table 1. As seen by inspection of the relevant data, whereas some features associated with the In_2O_3 appear in the as-deposited film, the peak positions are shifted from the reported values. This observation can be interpreted in terms of changes in the lattice constant of the material because doping of In_2O_3 with SnO_2 leads to an increase of the value for In_2O_3. An alternative explanation relies on the incorporation of Sn^{2+} ions in interstitial lattice positions that expand the In_2O_3 lattice (Beena et al. 2007). In addition, the observed narrowing of the peak width as the annealing temperature increases suggests a change in the grain size with larger crystals at the highest annealing temperature.

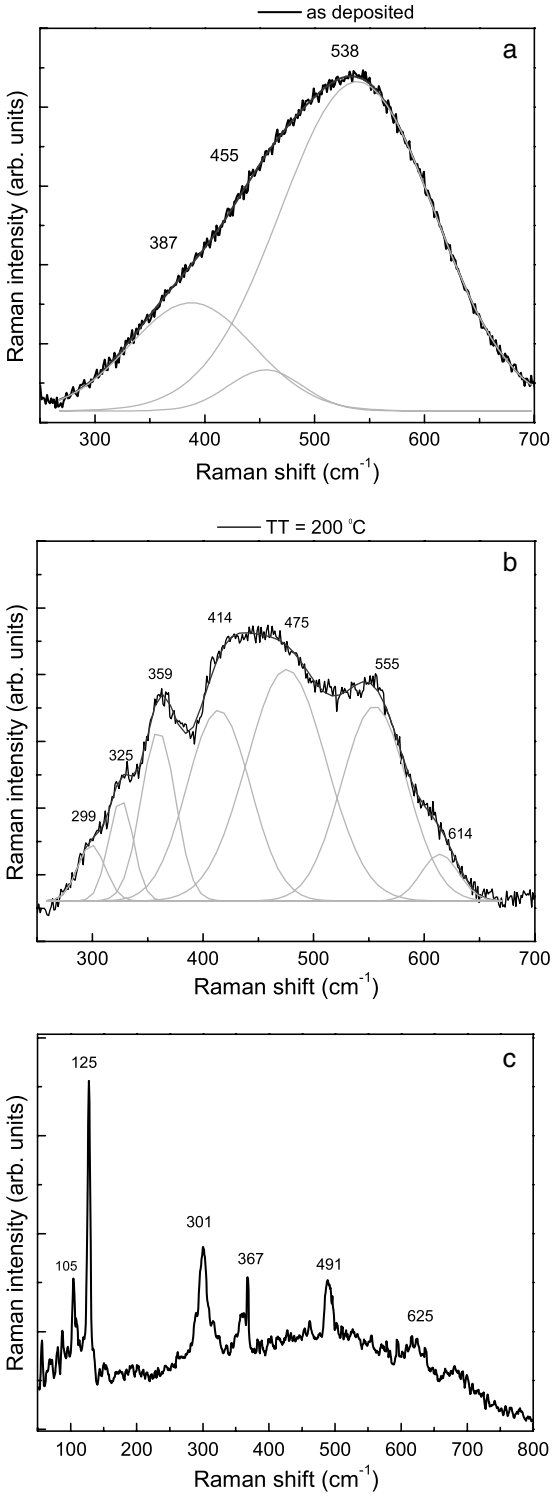


Fig. 2. Raman spectra of ITO films on flat surface (a) as deposited, (b) annealed at 200°C, and (c) annealed at 400°C by 1 hr deposition time; 1×10^{-2} Torr working pressure; oxygen-argon atmosphere

Fig. 3 shows a typical diffraction pattern of an ITO film prepared on a flat surface and annealed at 400°C for 1 h (the structural characterization was not made on the 600 μm optical fibers because of measuring problems associated to their particular geometry). Whereas the presence of peaks at $2\theta = 21.5$, 30.5, 35.4, and 50.9° can be assigned to the planes (211), (222), (400), and (440) of the cubic In_2O_3 bixbyte lattice structure, literature reports

Table 1. Raman Frequencies of the ITO Films Annealed at Different Temperatures on Flat Surface (data from Rogozin et al. 2006, p. 197)

ITO_{TT0} As deposited	ITO_{TT1} 100°C	ITO_{TT2} 200°C	ITO_{TT3} 300 °C	ITO_{TT4} 400 °C	Reported (In_2O_3)*
				105	117
				125	130
		299		301	308
329		325	321		
	387	359	363	367	365
		414			
475	455	475	460	491	490
557	538	555	556		
		614	581	625	637
			760		

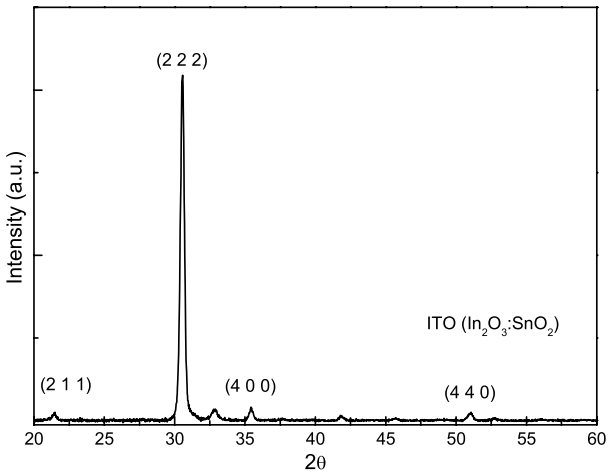


Fig. 3. ITO thin film XRD pattern on flat surface annealed at 400°C by 1 hr

(Raoufi et al. 2007) indicate that for a randomly oriented polycrystalline material the I_{400}/I_{222} ratio is approximately 0.3. From Fig. 3 it was found that $I_{400}/I_{222} = 0.05$, suggesting that the ITO film is highly oriented in the (222) plane direction. The width of the (222) peak on the other hand, was used to estimate the crystallite size by using the Debye-Scherrer equation, $D = 0.9\lambda/\beta 2\theta \cos\theta_{max}$. The calculated sizes were in the range from 22 to 29 nm defining a nanostructured ITO film. From diffraction experiments it was also possible to estimate the lattice constant *a*for the cubic phase resulting in a value of $a = 11.7$ Å, which is larger than that reported for pure indium oxide ($a = 10.12$ Å, Beena et al. 2007; Khodorov et al. 2007). The lattice constant difference results from the fact that the ionic radius of Sn^{2+} ions (0.93 Å) is larger than that of In^{3+} ions (0.79 Å), so the substitution or interstitial positioning of Sn^{2+} for In^{3+} ions should result in lattice expansion. This variation also confirms the observed effect in Raman spectroscopy experiments, i.e., the substitutional incorporation of Sn^{2+} ions into In^{3+} sites and/or the incorporation of Sn^{2+} ions in interstitial positions of the strucure (Beena et al. 2007; Wu et al. 1997).

Optical Characterization

As shown in Fig. 4, the optical transmittance of the deposited films in the spectral region from 300 to 1,100 nm is approximately 85% (characterization on flat surface). The inset in this Fig. 4 reveals the

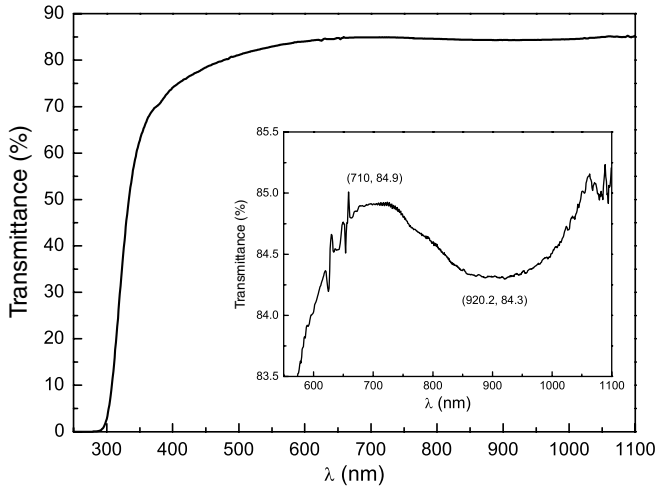


Fig. 4. Optical transmittance of the ITO thin film on flat surface in the spectral region 300 to 1,100 nm

presence of maxima and minima because of interference effects. From the UV-Vis spectra, the refractive index (1.9, using Goodman's model (Goodman 1978)) and the thickness of the films (from 70 to 497 nm depending on the deposition time) were determined. The E_g of the samples was computed by fitting the data to the Tauc equation, $\sqrt{\alpha(\omega)\eta\omega} = B\,(\eta\omega - E_g)$ (Tauc et al. 1966). The common procedure for the Tauc gap determination consists on plotting $(\alpha h\nu)^2$ as a function of photon energy, and extrapolating the linear portion of the curve to the zero absorption condition to obtain the value of the optical band gap ($E_g = 3.6$ eV). The calculated refractive index and band gap values are in good agreement with those reported in the literature for ITO (Fachun et al. 2007, Viespe et al. 2007).

Electrical Characterization

The resistivity of the prepared films was determined from electrical resistance measurements carried out by using the 4-point method. In all cases, ohmic behavior was observed. Fig. 5 shows the resistivity as a function of the annealing temperature. Inspection of this Fig. 5 reveals that as the annealing temperature increases, the resistivity decreases on the flat surface (from 4.4×10^{-2} to 5.6×10^{-4} Ω·cm). These values are smaller than those obtained for films deposited by RF sputtering (Wu et al. 1993) and are in good agreement with those measured for PLD deposits (Nisha et al. 1993). On the other hand, the resistivity of the films prepared on the optical fiber was around 1×10^{-3} Ω·cm. In addition, the resistivity of the films was determined from EIS measurements as described in the experimental section. The values obtained ranged from 2.2×10^{-2} to 7.4×10^{-3} Ω·cm showing good agreement with those obtained by using the 4-point method. Resistivity control in ITO films is a key issue depending on the foreseen application. In catalytic applications, a material with a low resistivity value is desired because the film is used as a conductive component; for sensing applications, a more resistive material is suitable because in this case changes in resistivity are monitored.

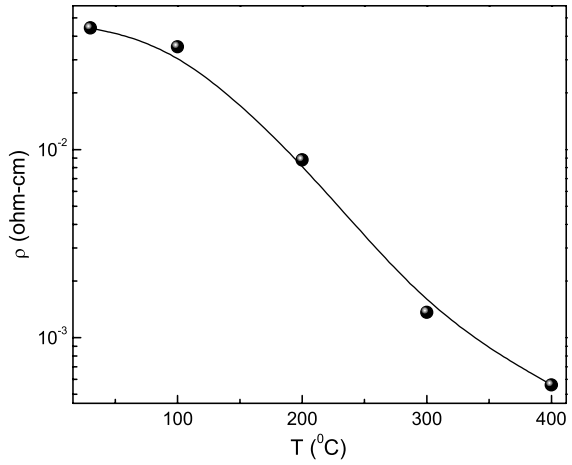


Fig. 5. Resistivity of the ITO thin film as function of the annealing temperature on a flat surface

Morphological Characterization

As shown in Figs. 6(a) and 6(b), scanning electron microscopy images of the deposited thin films on optical fibers showed smooth surfaces with a small number of scattered particles. The RMS surface roughness from atomic force microscopy analysis was 1.6 nm for samples deposited for 5 min. On the other hand, it is well known that splashing of droplets or particles on the film surface is one of the drawbacks of the laser-ablation technique. However, the microscopy images seem to indicate that under the deposition

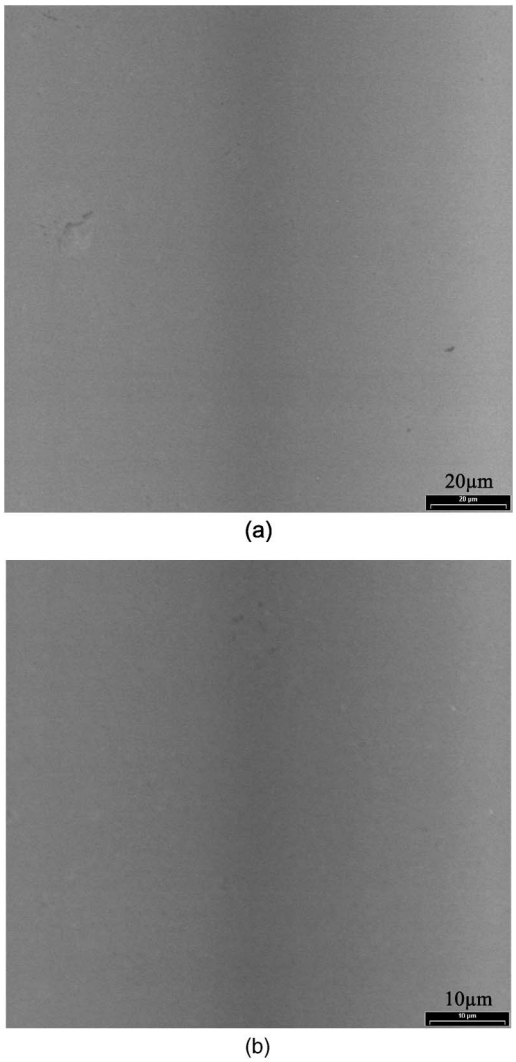


Fig. 6. SEM image of an ITO thin film on an optical fiber surface (a) 750X and (b) 1,500X

conditions used in this study, the accumulation of particulates is not a problem. Additionally, the EDS analysis only revealed the presence of the elements that compose the film, i.e., In, Sn, and O.

Electrochemical Characterization

Electrochemical characterization of the films was performed in a 0.05 M Na_2SO_4 pH 3 buffer as described in the experimental section. The TiO_2/ITO bilayers were prepared on both surfaces (flat and optical fiber) and characterized by cyclic voltammetry. Our experiments showed [see Fig. 7 (ii, iii) and Fig. 8 (ii, iii)] that in both cases it is possible to observe a UV light promoted increase in the current density of the hydrogen desorption process (−0.55 V versus Hg/Hg_2SO_4) (Esquivel et al. 2009; Peill and Hoffman 1995; Wang and Ku 2003, Danion et al. 2007). As opposed to the previously explored approach that considered a SnO_2 : Sb conductive film prepared by the painting technique that results in a poorly anchored conductive film that suffers electrical disconnection after 10 cycles, the TiO_2/ITO film prepared by the PLD technique showed good electrochemical stability after 20 cycles.

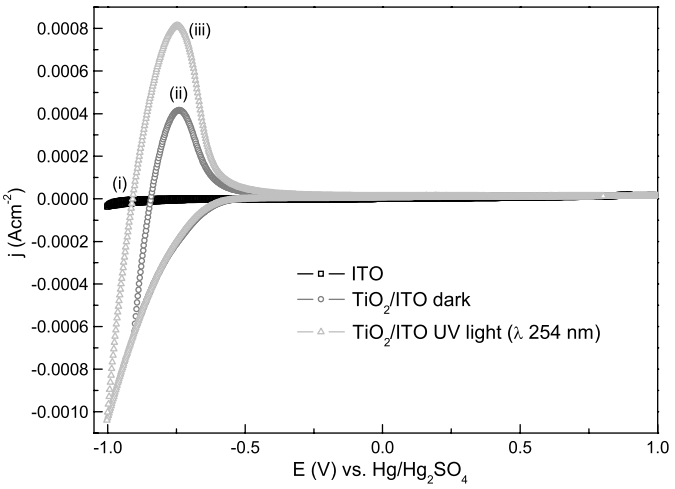


Fig. 7. (i) Voltamperogram of an ITO film on flat surface; (ii) electrochemical response of a sample of ITO on glass with TiO_2 in the absence and (iii) in the presence of UV light in Na_2SO_4 0.05 M electrolyte pH 3 and nitrogen atmosphere

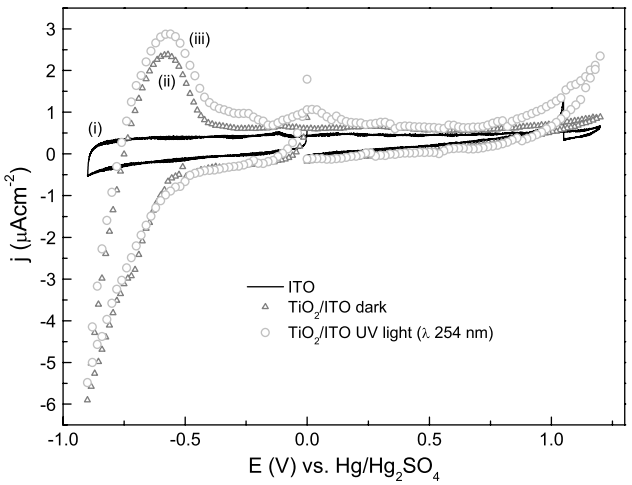
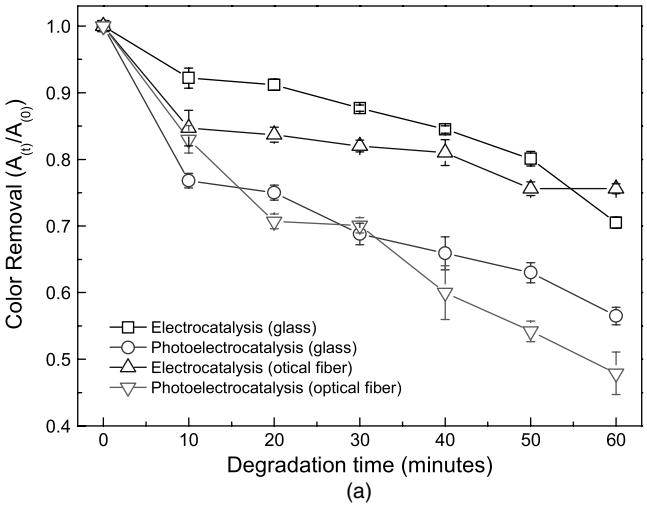


Fig. 8. (i) Voltamperogram of an ITO film on an optical fiber surface, (ii) covered with TiO_2 in the absence and (iii) in the presence of UV light in Na_2SO_4 0.05 M electrolyte pH 3 and nitrogen atmosphere

Photoanode Performance for Wastewater Treatment

To evaluate the efficiency of the electrodes as photoanodes, we tested them in the removal of color and TOC from an Orange II dye aqueous solution (15 mgL^{-1}). In the degradation tests, while in the flat glass substrate the illumination source was located outside the electrochemical cell pointing directly to the face covered with TiO_2, in the optical fiber light was introduced coupling one end of the fiber to the light source. The later illumination arrangement has the advantage that light impinges directly over the catalyst material avoiding absorption and/or scattering of the radiation by the reaction medium or the construction material of the cell. In this case, the optical fiber works as electrode, light distributor and TiO_2 support (Esquivel et al. 2009).

From degradation tests, it was possible to measure color and TOC removal versus degradation time [Figs. 9(a) and 9(b)]. In the electrocatalytic process (no illumination), it was not possible to observe a significant difference in color removal when the flat or the optical fiber surfaces were employed (30 and 25%, respectively). When the



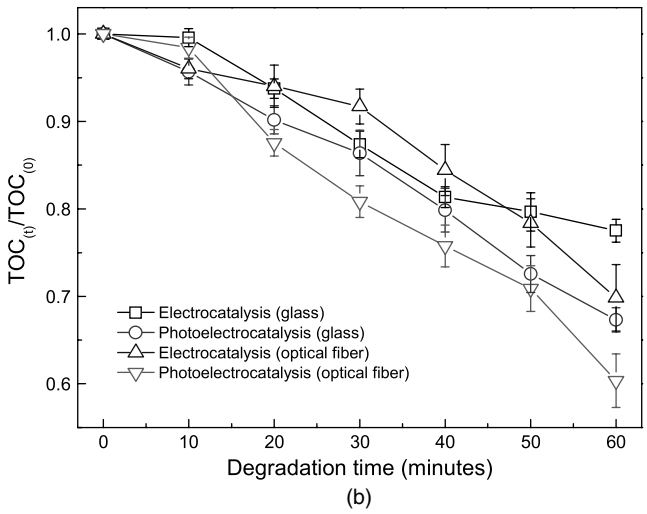


Fig. 9. (a) Color and (b) TOC removal by electrocatalysis and photoelectrocatalysis using glass and optical fiber surfaces; Na_2SO_4 0.05 M pH 3 electrolyte; oxygen atmosphere; 15 mgL^{-1} orange II; 1 mAcm^{-2} cathodic current

system is photoassisted on the other hand, the average measured values show a clear difference in color removal kinetics between the two anode geometries surveyed [Fig. 9(a)]. In this way, when UV light is delivered to the system, the optical fiber is characterized by a better color removal performance (56%) when compared to that of the flat anode (44%).

TOC removal experiments showed that, as expected, there is a difference between the electrocatalytic and the photoassisted processes, but in these experiments a difference between the optic fiber cylindrical and flat geometries could not be observed. By using the average values of five measurements as described in the experimental section, however, there is a difference of approximately 10% between the two substrates (23% with the flat and 30% with the optical fiber surface) when the system works as electrocatalytic. A difference that is similar to that obtained from a comparison of the performance between the two photoanode substrates after 60 min under UV illumination (while the TOC removal value with an optical fiber is 40%, that of a flat surface is 33%).

Conclusion

Our results show that it is possible to obtain ITO thin films over different substrate shapes by using the PLD technique, and that these modified substrates can efficiently be used as photoanodes for photoelectrocatalityc applications. The deposited materials were tested by using electrocatalytic and photoelectrocatalytic processes, with improved results in the later case. Also, the prepared TiO_2/ITO bilayers on optical fibers showed an average better performance than those deposited on flat glass substrates as indicated by color removal experiments of a model Orange II dye solution. This result suggests that the illumination configuration has an effect over the color removal parameters that characterize the performance of a flow electrochemical reactor.

Acknowledgments

The writers thank the Mexican Council for Science and Technology (CONACyT, Grant no. SEP-CONACYT 83894) for financial support of this work. K.E.E. also acknowledges CONACyT for a graduate fellowship.

Notation

The following symbols are used in this paper:

B = constant;
D = grain crystal size (nm);
E_g = optical band gap energy;
$h\nu$ = photon energy;
I = intensity;
P = pressure;
α = optical absorption coefficient;
β = FWHM peak;
λ = wavelength;
λ^* = wavelength of the Cu K_α radiation (0.15406 nm);
θ = diffraction angle; and
Ω = ohm.

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Queries

1. Please check that ASCE Membership Grade Marks (M.ASCE, etc.) are provided for all authors that are members.
2. We have defined pH as hydrogen ion concentration. Is this correct?
3. The Mohammed et al. 2004 reference was changed to Mollah et al to reflect a change to the author names in the actual reference. Please review the reference and confirm that this change is correct.
4. This is the first use of TOC, defined as "toxic organic compound" but several paragraphs down, TOC is defined as "total organic carbon." Which version should be used as TOC and which should remain spelled out to avoid confusion if they are different terms?
5. We changed Kulkami et al. 1998 to Kulkarni et al. 1999 to match the citation in the reference list. Is this correct?
6. TOC is begin defined here as "total organic carbon," but has already been defined earlier in the paper as "toxic organic compound." Which one should be used for TOC, and if they are different, which one should remain spelled out within the article?
7. Martínez-Huitle et al 2009 was changed to Martínez-Huitle and Brillas 2009 to match the existing citation in the reference list. Is this correct?
8. Exactly what is being attributed to Lesker Co.? Are they the maker of the laser beam or the target? May we rephrase the sentence to read "The Lesker Co. laser beam focused onto a rotating high purity indium oxide-tin oxide (90–10%) target." Or "...(90–10% Lesker Co. target."?
9. ASCE style requires SI units. Can you please convert "1×10^{-5} Torr" for expression in Pa? Or offer the SI alternative to be used as well.
10. ASCE style requires SI units. Can you please convert "1×10^{-2} Torr" for expression in Pa? Or offer the SI alternative to be used as well.
11. ASCE style requires SI units. Can you please convert "$\lambda^* = 1.5406$ Å: for expression in nm? Or offer the SI alternative to be used as well.
12. Are there any authors in the reference list that should be cited in the "ITO Plasma Laser Deposition and Characterization" section. If so, please note where the citations should go in the paragraph.
13. In the "TiO_2/ITO Bilayer Construction" section, Manriquez et al. 2007 was changed to Manriquez and Godínez 2007 both times to match the reference list. Is this correct?
14. Which TOC are you using here: toxic organic compound or total organic carbon?
15. In the Fig. 2 caption, can you please convert "1×10^{-2} Torr" for expression in Pa? Or offer the SI alternative to be used as well.
16. There is an asterisk in the the header of the last column in Table 1. Was there supposed to be a footnote? Or can we delete that asterisk?
17. Please confirm that slashing the fractionI_{400}/I_{222} did not change the meaning.
18. Please confirm that slashing the fraction$I_{400}/I_{222} = 0.05$ did not change the meaning.
19. Please confirm that slashing the fraction$D = 0.9\lambda/\beta 2\theta \cos\theta_{\max}$ did not change the meaning.
20. ASCE style requires SI units. Can you please convert "$a = 11.7$ Å" for expression in nm? Or offer the SI alternative to be used as well.
21. ASCE style requires SI units. Can you please convert "$a = 10.12$ Å" for expression in nm? Or offer the SI alternative to be used as well.
22. ASCE style requires SI units. Can you please convert "(0.93 Å)" for expression in nm? Or offer the SI alternative to be used as well.
23. ASCE style requires SI units. Can you please convert "(0.79 Å)" for expression in nm? Or offer the SI alternative to be used as

well.

24. There are currently two Wu et al. 1997 references in the list. Should this use be 1997a, 1997b, or both. 1997b is not currently cited in the article.

25. Please supply a definition for RF.

26. Wu et al. 1993 does not exist in the reference list. Please provide a new reference or correct citation to match an existing one.

27. Isn't the use of deposits here redundant: PLD deposits? May I delete "deposits" from the sentence.

28. Nisha et al. 1993 does not exist in the reference list. Should this be Nisha et al. 2005 (which is not currently cited in the article) or is there a new reference?

29. Can you please supply the full section title you mean when you say "experimental section"?

30. We changed Peill et al. 1995 to Peill and Hoffman 1995 to match the existing reference in the list. Is that correct?

31. Which TOC are you using in this section: toxic organic compound or total organic carbon?

32. Please provide the full section name when you refer to "the experimental section."

33. The last sentence in this section is incomplete; there is no verb to go with the text prior to the parenthetical note. Please review the entire sentence.

34. Please supply a definition for FWHM.

35. ASCE style requires issue numbers with journal citations where available. Please provide an issue number for Beena 2007

36. Please confirm author names for Chiou 1999 and supply an issue number.

37. Please provide an issue number for Choi 2003

38. Please provide an issue number for Danion 2004.

39. Please provide an issue number for Danion 2007.

40. This query was generated by an automatic reference checking system. This reference (Elangovan, E., and Ramamurthi, K. [2003]) could not be located in the databases used by the system. While the reference may be correct, we ask that you check it so we can provide as many links to the referenced articles as possible.

41. Please provide an issue number for Esquivel 2009.

42. Please provide an issue number for Fachun 2007.

43. Please supply an issue number for Goodman 1978.

44. Please supply an issue number for Guido 2004.

45. Please supply an issue number for Johnson 2000.

46. Please supply an issue number for Khodorov 2007.

47. Please supply an issue number for Kim et al. 2000.

48. Please supply an issue number for Kim 2006.

49. Please supply an issue number for Kulkarni 1999.

50. Please supply an issue number for Li 2000.

51. Please confirm author names and supply an issue number for López et al. 2004.

52. Please confirm author names and supply an issue number for Manriquez et al. 2007.

53. Please confirm author name and supply an issue number for Mollah et al. 2007.

54. Please supply an issue number for Moore et al. 2006.

55. A check of online databases revealed a possible error in this reference. (Ngaffo, F., Caricato, A. P., Fernandez, M., Martino, M., and Romano, F. [2007]) The date has been changed from '2003' to '2007'. Please confirm this is correct.

56. Nisha et al. 2005 is not currently cited in the article. Please update the in-text citation previously noted, add a new citation in the article, or delete this reference from the list.

57. Please supply an issue number for Peill et al. 1995.

58. Please supply an issue number for Peralta-Hernández et al. 2007.

59. Please supply an issue number for Prem et al. 1980.

60. Please supply an issue number for Raoufi et al. 2007.

61. Please supply an issue number for Rogozin et al. 2007.

62. Please supply an issue number for Tauc et al. 1966.

63. Please supply an issue number for Viespe et al. 2007.

64. Please supply an issue number for Vinodgopal et al. 1993.

65. A check of online databases revealed a possible error in this reference. (Wang, W., and Ku, Y. [2003]) The volume has been changed from '59' to '50'. Please confirm this is correct.

66. Please supply an issue number for Wang and Ku 2003.

67. Please supply an issue number for Wu and Chiou 1997a.

68. W7 and Chiou. 1997b is not currently cited in the article. Please update the in-text citations previously noted, add a new citation in the article, or delete this reference from the list. If the reference stay s as is, please supply an issue number for Wu and Chiou 1997b.

69. Please supply an issue number for Yong 2008.

70. Please supply an issue number for Yong 2007.

71. Please supply an issue number for Zhang 2003.

72. Please supply an issue number for Zhang 2008.