Production and Characterization of Boron Doped Diamond Electrodes Grown on Titanium Applied to Textile Dye Degradation

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Summary

• Introduction
• Objectives
• BDD/Ti Electrode: Production and Characterization
• Electrochemical Degradation of RO16 Dye
• Conclusions
Motivation

INPE’s Mission

National Institute for Climate Changes (CNPq/Fapesp)

Material development

Environmental monitoring

Diamond electrodes for waste water treatment
Introduction

Environmental Pollution

• Inappropriate use of environmental resources.
• Population increase.
• Industrial activities increase.
Introduction - Synthetic Organic Dyes

- Widely used in textile industry;
- High stability under sunlight;
- Resistant to microbiological attack;
- Carcinogenic, mutagenic and bactericide properties.

Environmental Impact

Removal of organic pollutant is a technological challenge
Introduction – Advanced Oxidation Process (AOP)

- High efficiency to decompose organic compounds
- Oxidation processes that produce hydroxyl radical (•OH) to transform the pollutants into carbon dioxide using reagents such as chlorine, hydrogen peroxide...
- Electrochemical Method (EAOP)
- (•OH) production from Electrochemical Clean reagent “the electron”
- The suitable anodic material???

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**Introduction – BDD/Ti Electrodes**

**BDD Properties**
"Non-active anode"

- High O\textsubscript{2} overpotential to produce (•OH) (wide potential window);
- High electrochemical stability in corrosive electrolytes;
- Boron doping from $10^{17}$ to $10^{22}$ B cm\textsuperscript{-3}.

**Titanium Properties**

- Relatively high conductivity;
- Attainable for large area;
- Low cost compared to Ta, Ni, and W;
- Good mechanical resistance to handling;
- Specially, its corrosion resistance due to the formation of a titanium oxide layer.

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Introduction – Reactive Orange 16 Dye (RO16)

- Complex molecule;
- Textile azo-dye (-N=N-) widely used in industry;
- Biologically refractory and resistant to degradation.
Objectives

- BDD/Ti growth with high quality and adherence (challenge!!);
- BDD/Ti electrodes with different thickness and boron doping level;
- The application of BDD/Ti electrode on the RO16 dye electrochemical degradation;
- The use of analytical techniques to monitor the RO16 dye concentration during the process.
BDD/Ti Growth - HFCVD Technique

Reactants

\[ \text{H}_2 + \text{CH}_4 \quad 99:1 \]

Activation

\[ \text{H}_2 \xrightarrow{\Delta} 2\text{H} \cdot \\
\text{CH}_4 + \text{H} \cdot \rightarrow \text{CH}_4 \cdot +\text{CH}_2 \cdot +\text{CH}_3 \cdot +\text{H}_2 \]

Flow and Reaction

Diffusion

Substrate

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BDD/Ti - SEM Characterization

Doping level
Estimated from Raman

<table>
<thead>
<tr>
<th>samples</th>
<th>Acceptor concentration (B cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3.0 x 10$^{20}$</td>
</tr>
<tr>
<td>II</td>
<td>7.0 x 10$^{20}$</td>
</tr>
<tr>
<td>III</td>
<td>1.0 x 10$^{21}$</td>
</tr>
</tbody>
</table>
BDD/Ti - Raman Characterization

7 h

24 h
Electrochemical Degradation of the RO16 Dye

Electrolytes: 
K₂SO₄+H₂SO₄ (0.1 mol L⁻¹) + RO16 (50 mg L⁻¹) 
J = 25, 50, 75, 100, 150, e 
200 mA cm⁻². 
90 min; 20 °C; 350 mL
Electrochemical Degradation – BDD/Ti - 7 h - doping levels of I, II, and III

- 25 mA cm\(^{-2}\)
- 200 mA cm\(^{-2}\)

The best result
TOC Removal and HPLC—BDD/Ti of 7 h

200 mA cm$^{-2}$

HPLC at 254 nm $\pi - \pi^*$ transition of aromatic compounds
(1) Untreated solution—peaks from A to F;
(2) 10 min of treatment;
(3) 90 min of treatment: disappearance of the two main peaks related to the dye (D and F).

<table>
<thead>
<tr>
<th>Acceptor concentration (B.cm$^{-3}$)</th>
<th>% TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>25 %</td>
</tr>
<tr>
<td>II</td>
<td>45 %</td>
</tr>
<tr>
<td>III</td>
<td>35 %</td>
</tr>
</tbody>
</table>

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UV-VIS comparative results – BDD/Ti samples type II

7 h - 200 mA cm$^{-2}$

24 h - 200 mA cm$^{-2}$
TOC Removal and HPLC – BDD/Ti sample type II – 24 h

HPLC at 254 nm $\pi - \pi^*$ transition of aromatic compounds
(1) Untreated solution – peaks from A to F;
(2) 10 min of treatment: peak F already disappeared;
(3) 90 min of treatment: complete disappearance of the two main peaks related to the dye (D and F).

<table>
<thead>
<tr>
<th>Deposition time (h)</th>
<th>% TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>45 %</td>
</tr>
<tr>
<td>24</td>
<td>50 %</td>
</tr>
</tbody>
</table>
Conclusions

- The BDD/Ti electrodes with different thickness and doping levels without cracks or delaminations were obtained with success;

- The UV/VIS, TOC, and HPLC showed that all BDD/Ti electrodes were effective in the color and TOC removal of the RO16 dye.

- The enhancement of the dye degradation was observed with the optimized parameters: doping level as well as the diamond film thickness. (Why???)
Acknowledgements
Thank you !!!